Supporting Information for

Increasing Materials' Response to Two-photon NIR Light via Self-immolative Dendritic Scaffold

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Abbreviations. DCM (dichloromethane), TFA (trifluoroacetic acid), EtOAc (ethyl acetate), DMF (dimethyl formamide), DMSO (dimethyl sulfoxide), DIEA (N, N-diisopropylethyl amine), RT (room temperature).

General Methods and Instrumentation. Flash chromatography was performed using a CombiFlash Companion system. ^{1}H NMR spectra were acquired using a Joel 500 MHz spectrometer or a Varian 400 MHz spectrometer. ^{13}C NMR spectra were acquired using a Varian spectrometer operated at 100 MHz. Purity of the new compounds and degradation of the dendrimers was monitored by an Agilent 1200 HPLC equipped with PDA and MSD detectors and a C18 column with 0.1 % formic acid/H_2O and 0.1 % formic acid/acetonitrile as eluents at a flow rate of 0.4 mL/min. A Ti:Sapphire laser (Mai Tai HP, Spectra Physics) with ~100 fs pulse widths and 80 MHz repetition rate generated light for NIR irradiation. For dendrimers' degradation by NIR irradiation, 2.5 W (4 kW/cm^2) of 740 nm light was focused into the solution using a EFL 33.0 mm lens. The 50 μL quartz cells with 3 mm path length were used. The Amplex Red Glutamic Acid assay kit was purchased from Invitrogen and the analysis was performed according to the manufacturer's protocol. The fluorescence spectra were acquired on FluoroLog-3 spectrophotometer (JY Horiba, Inc.)

For all dendrimers, the irradiation experiments followed by injection into HPLC and Amplex Red analysis were performed in triplicate to obtain standard deviation values.

Compounds **1** and **3** were synthesized according to ref. 1.

Compound **2**. Glutamate hydrochloride (0.26 g, 1.23 mmol) was dissolved in 10 mL dry DMF and 0.42 mL of DIEA (2.4 mmol) was added dropwise. Compound **1** was added and reaction was heated to 50˚C and monitored by HPLC. After 2 hours the reaction mixture was cooled to RT and solvent was removed on rotary evaporator. The residue was dissolved in ethyl acetate (EtOAc) and the precipitate was filtered out. The solvent was removed on a rotary evaporator. The product was isolated by flash-chromatography (silica gel, Hexane/EtOAc gradient). Yield: 0.28 g (53%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (s, 1H), 7.15 (s, 1H), 6.37 (s, 1H), 5.80 (d, J=10 Hz, 1H), 5.31 (s, 2H), 5.23 (s, 2H), 4.42 (m, 1H), 3.78 (s, 3H), 3.68 (s, 3H), 3.51 (s, 3H), 2.43 (m, 2H), 2.24 (m, 1H), 2.05 (m, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.12, 171.90, 160.13, 154.07, 148.57, 127.42, 112.38, 111.10, 108.48, 103.98, 95.08, 61.64, 56.66, 53.52, 52.73, 51.94, 29.88, 27.25 ppm.

HRMS: composition: $C_{20}H_{22}BrNO_{10}Na$; mass measured: 538.0320; theor. mass: 538.0319; delta: 0.2 ppm.

Purity by HPLC: 96.77% at 254 nm; 98.77% at 320 nm; 98.86% at 280 nm.

G0. Compound **2** (0.1 g, 0.194 mmol) was dissolved in 2 mL of DCM/TFA (1/1) and stirred for 30 min. The solvents were removed on rotary evaporator. The residue was dissolved in 6 mL MeOH/H_2O (5/1) and cooled to 0˚C. 10 M NaOH solution was added dropwise until the reaction mixture turned yellow. The reaction was allowed to warm to RT and the progress was monitored by HPLC (C-18 Zorbax column, H_2O/can gradient). After completion, the reaction mixture was neutralized with 10 M HCl to pH 5. MeOH was removed on rotary evaporator and aqueous fraction was extracted with EtOAc and dried over Na_2SO_4. After removal of EtOAc the product was purified by flash-chromatorgaphy (C-18, H_2O/MeOH gradient). Yield: 0.038 g (40%). ^{1}H and ^{13}C NMR matched with the data reported in ref. 2.

HRMS: composition: $C_{16}H_{13}NO_9Br$; mass measured: 441.9777; theor. mass: 441.9779; delta: 0.5 ppm.

Compound **4**. Compound **3** (2 g, 2.8 mmol) was dissolved in a mixure of 10 mL dry DMF anf 0.93 mL (6.72 mmol) Et_3N at RT. A solution of glutamate hydrochloride (1.42 g, 6.72 mmol) in 5 mL dry DMF was added dropwise and the reaction mixture was placed in oil bath at 50˚C. The progress of reaction was followed by HPLC (C-18 Zorbax column, H_2O/can gradient). After 3 hours the reaction mixture was cooled to RT and 20 mL EtOAc was added. The inorganic precipitate was filtered out. The solvents were removed on rotary evaporator. The product was isolated by flash-chromatography (silica gel, Hexane/EtOAc gradient). Yield: 1.8 g (85%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20 (s, 2H), 5.61 (m, 2H), 5.02 (s, 2H), 4.36 (t, J=5 Hz, 2H), 3.73 (s, 6H), 3.65 (s, 6H), 3.6-3.45 (m, 4H), 3.14-2.90 (m, 6H), 2.50 (m, 4H), 2.40 (s, 3H), 2.23 (m, 2H), 2.01 (m, 2H), 1.64 (m, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.19, 172.37, 155.92, 135.87, 131.06, 130.72, 129.33, 62.43, 53.39, 52.64, 51.94, 47.33, 46.28, 35.53, 34.99, 30.04, 28.53, 27.67, 21.00 ppm.

HRMS: composition: $C_{35}H_{52}N_4O_{16}Na$; mass measured: 807.3269; theor. mass: 807.3271; delta: 0.2 ppm.

Purity by HPLC: 95.8% at 254nm; 95.5 at 280 nm.

Compound **5**. Compound **4** (0.35 g, 0.446 mmol) was stirred in 2 mL of DCM and TFA (1/1) mixture for 30 min at RT. The solvents were removed on rotary evaporator, the residue was redissolved in 5 mL DMF and 2 mL of Et_3N. Compound **1** (0.312 g, 0.670 mmol) was added and the reaction the mixture was stirred overnight at 50˚C. After completion of reaction the mixture was cooled to RT, diluted with EtOAc

and inorganic precipitate was filtered out. The solution was dried over Na_2SO_4. The solvents were removed on rotary evaporator. The product was isolated by flash-chromatography on silica gel with Hexane/EtOAc gradient. Yield: 0.306 g (63%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84 (s, 1H), 7.16 (m, 3H), 6.36 (s, 1H), 5.30 (m, 4H), 5.02 (s, 4H), 4.36 (t, J=5 Hz, 2H), 3.72 (s, 6H), 3.64 (s, 6H), 3.52 (s, 3H), 3.70-3.45 (m, 4H), 3.16-3.04 (m, 6H), 2.39 (m, 4H), 2.32 (s, 3H), 2.04 (m, 2H), 1.85 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.15, 172.39, 160.45, 154.18, 149.38, 145.33, 135.96, 135.84, 130.23, 129.29, 129.20, 128.00, 112.69, 110.67, 108.52, 104.01, 95.24, 62.59, 62.33, 56.79, 53.37, 51.91, 46.78, 35.06, 35.03, 34.41, 30.02, 27.62, 20.96 ppm.

HRMS: composition: $C_{43}H_{53}BrN_4O_{20}Na$; mass measured: 1047.2331; theor. mass: 1047.2329; delta: 0.2 ppm.

Purity by HPLC: 96.52% at 254 nm; 97.68% at 320 nm; 96.71% at 280 nm.

Compound **6**. Compound **4** (1.2 g, 1.5 mmol) was stirred in 10 mL DCM/TFA (1/1) for 30 min at RT. Solvents were removed on rotary evaporator, the residue was dissolved in 3 mL DMF and 5 mL Et_3N was added. Compound **3** (0.5 g, 0.7 mmol) in 5 mL DMF was added and the reaction was stirred at 50˚C overnight. The solvents were removed on rotary evaporator and the product was isolated by flash-chromatography on silica gel with Hexane/EtOAc gradient. Yield: 1.2 g (95%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.19 (m, 6H), 5.01 (m, 12H), 4.35 (s, 4H), 3.72 (s, 12H), 3.64 (s, 12H), 3.70-3.25 (m, 12H), 3.14 – 2.78 (m, 18H), 2.37 (s, 9H), 2.39-2.25 (m, 8H), 2.20 (m, 4H), 1.97 (m, 4H), 1.45 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.05, 172.26, 162.68, 156.02, 153.99, 145.31, 135.72, 130.67, 130.19, 129.61, 129.18, 62.30, 53.30, 52.44, 51.76, 47.64-46.05, 36.50, 35.72-34.60, 31.42, 29.92, 28.38, 27.39, 20.84 ppm.

HRMS: composition: $C_{81}H_{114}N_{10}O_{36}Na$; mass measured: 1825.7284; theor. mass: 1825.7289; delta: 0.3 ppm.

Purity by HPLC: 95.22% at 254 nm; 95.21% at 280 nm.

Compound **7**. Compound **6** (0.5 g, 0.28 mmol) was dissolved in 4 mL DCM/TFA (1/1) and stirred at RT for 30 min. The solvents were removed on rotary evaporator and the residue was dissolved in 10 mL DMF/Et_3N (3/2). Compound **1** (0.163 g, 0.33 mmol) was added and the mixture was stirred at 50˚C overnight. The solvents were removed on rotary evaporator and the product was isolated by flash-chromatography on silica gel with EtOAc/MeOH gradient. Yield: 0.53 g (93%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (s, 1H), 7.16 (m, 7H), 6.33 (s, 1H), 5.31 (s, 4H), 5.00 (m, 12H), 4.34 (s, 4H), 3.71 (s, 12H), 3.63 (s, 12H), 3.51 (s, 3H), 3.70-3.19 (m, 12H), 3.14 – 2.75 (m, 18H), 2.31 (s, 9H), 2.39-2.25 (m, 8H), 2.17 (m, 4H), 1.96 (m, 4H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.03, 172.27, 160.29, 156.27, 155.87, 154.10, 153.80, 135.80, 130.52, 130.04, 129.58, 129.20, 127.81, 112.57, 108.43, 103.89, 95.13,62.22, 56.68, 53.31, 52.43, 51.75, 47.64-46.64, 35.69-34.47, 29.93, 27.35, 20.84 ppm.

HRMS: composition: $C_{89}H_{115}BrN_{10}O_{40}Na_2$; mass measured: 1044.3126; theor. mass: 1044.3120; delta: 0.6 ppm.

Purity by HPLC: 95.29% at 254 nm; 97.09% at 320 nm; 965.19% at 280 nm.

G1. Compound **5** (0.29 g, 0.28 mmol) was reacted with TFA (1 mL) in DCM (1 mL) for 30 min. The solvents were removed on rotary evaporator. The residue was dissolved in 10 mL MeOH/$H_2$0 (10/1) and 10 M NaOH (0.4 mL) was added. The reaction mixture was stirred at 0˚C for 10 hrs. After the reaction was completed, the solution was neutralized with 12 M HCl to pH 5. MeOH was removed on rotary evaporator and aqueous fraction was extracted with EtOAc. The product was purified by flash-chromatography using C-18 column and H_2O/MeOH gradient. Yield: 0.168 g (65%).

^{1}H NMR (500 MHz, CD_3OD): δ = 7.87 (m, 1H), 7.22 (m, 2H), 6.84 (s, 1H), 6.25 (m, 1H), 5.35 (m, 2H), 4.98 (s, 4H), 4.19 (m, 2H), 3.64-3.57 (m, 4H), 3.31-2.99 (m, 6H), 2.39 (t, J=5 Hz, 4H), 2.32 (s, 3H), 2.14 (m, 2H), 1.87 (m, 2H).

HRMS: composition: $C_{37}H_{41}BrN_4O_{19}Na$; mass measured: 947.1439; theor. mass: 947.144; delta: 0.2 ppm.

Purity by HPLC: 97.21% at 254 nm; 97.36% at 320 nm; 97.71% at 280 nm.

G2 was obtained from compound **7** (0.2 g, 0.098 mmol) according to the procedure described for **G1** above. Yield: 0.103 g (69%).

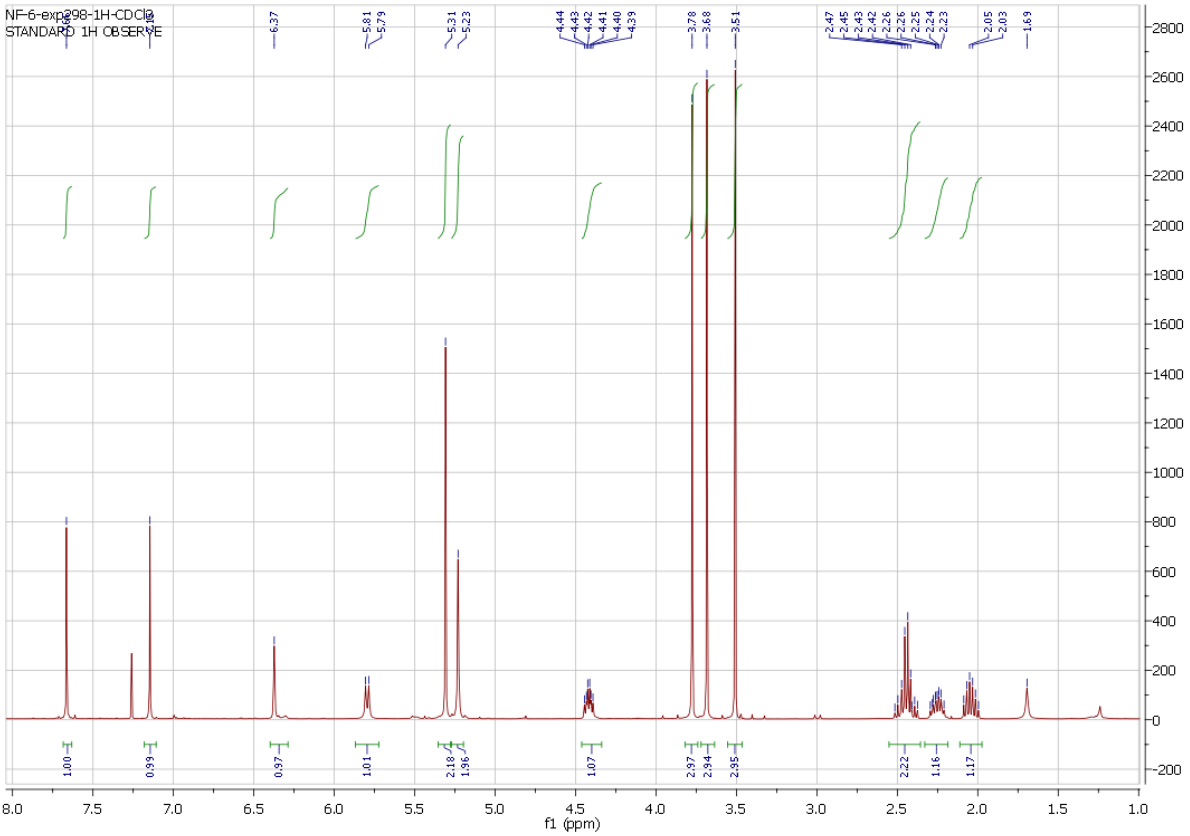
^{1}H NMR (500 MHz, $DMSO_{-d6}$): δ = 7.86 (m, 1H), 7.19 (s, 7H), 6.91 (s, 1H), 6.14 (m, 1H), 5.28 (s, 2H), 4.92 (s, 12H), 3.98 (m, 4H), 3.05-2.81 (m, 18H), 2.29 (s, 9H), 2.36 – 2.17 (m, 8H), 1.94 (m, 4H), 1.76 (m, 4H) ppm.

HRMS: composition: $C_{79}H_{95}BrN_{10}O_{39}Na_2$; mass measured: 966.2362; theor. mass: 966.2363; delta: 0.1 ppm.

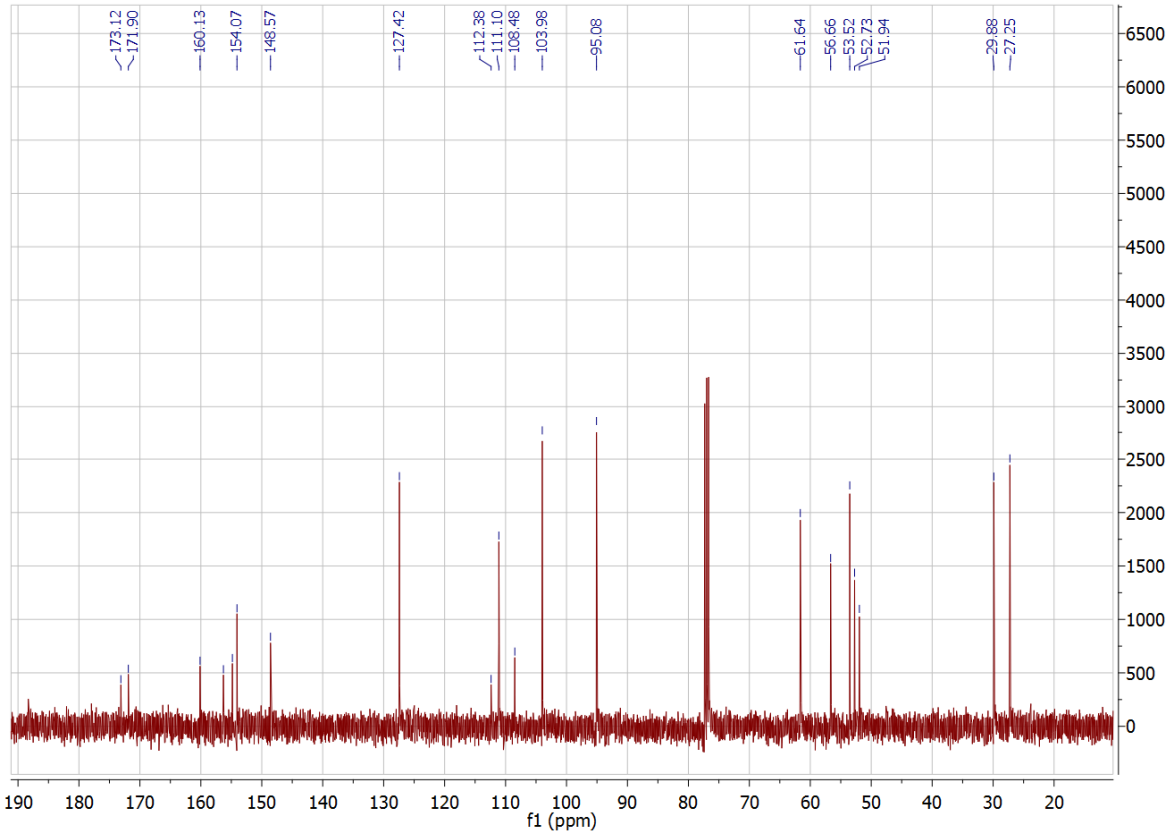
Purity by HPLC: 98.31% at 254 nm; 98.78% at 320 nm; 97.73% at 280 nm.

For **G1** and **G2**, the ^{13}C NMR spectra could not be acquired due to excessive peak broadening caused by hydrogen exchange.

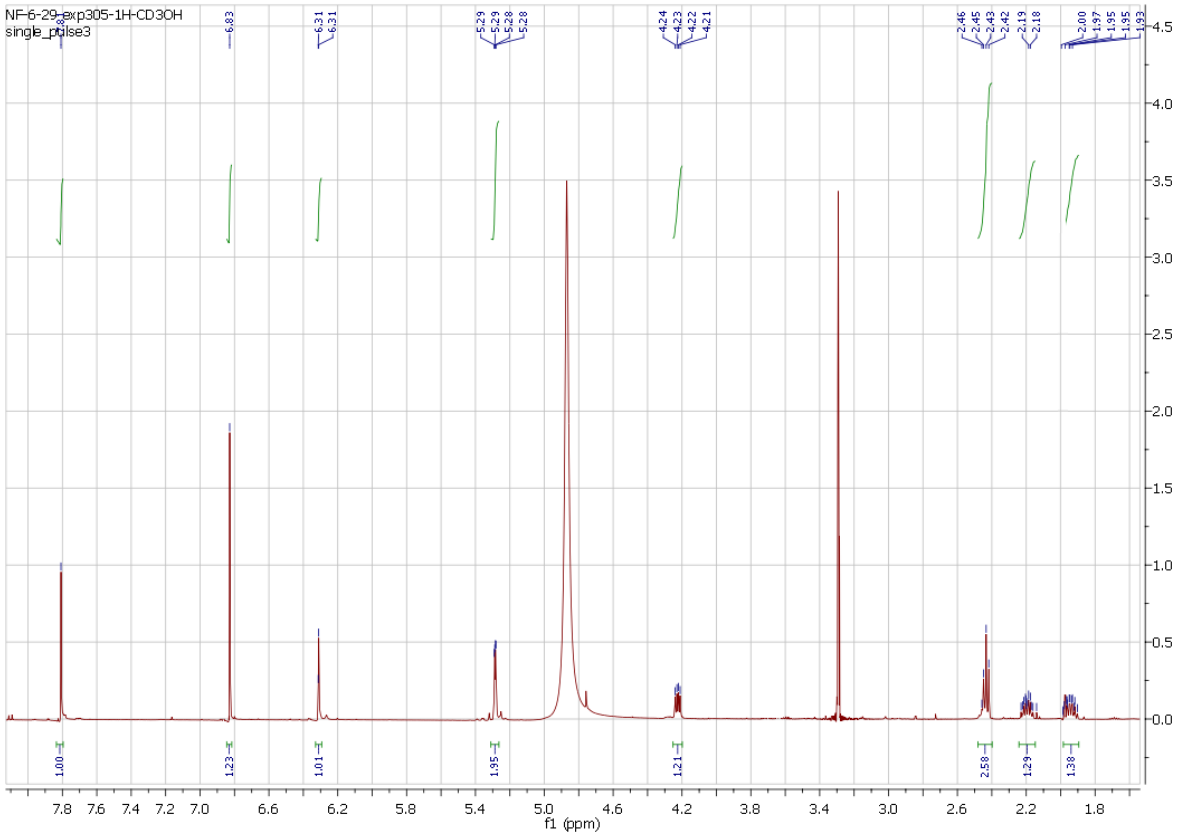
Compound 2. ^{1}H NMR ($CDCl_3$, 500 MHz)



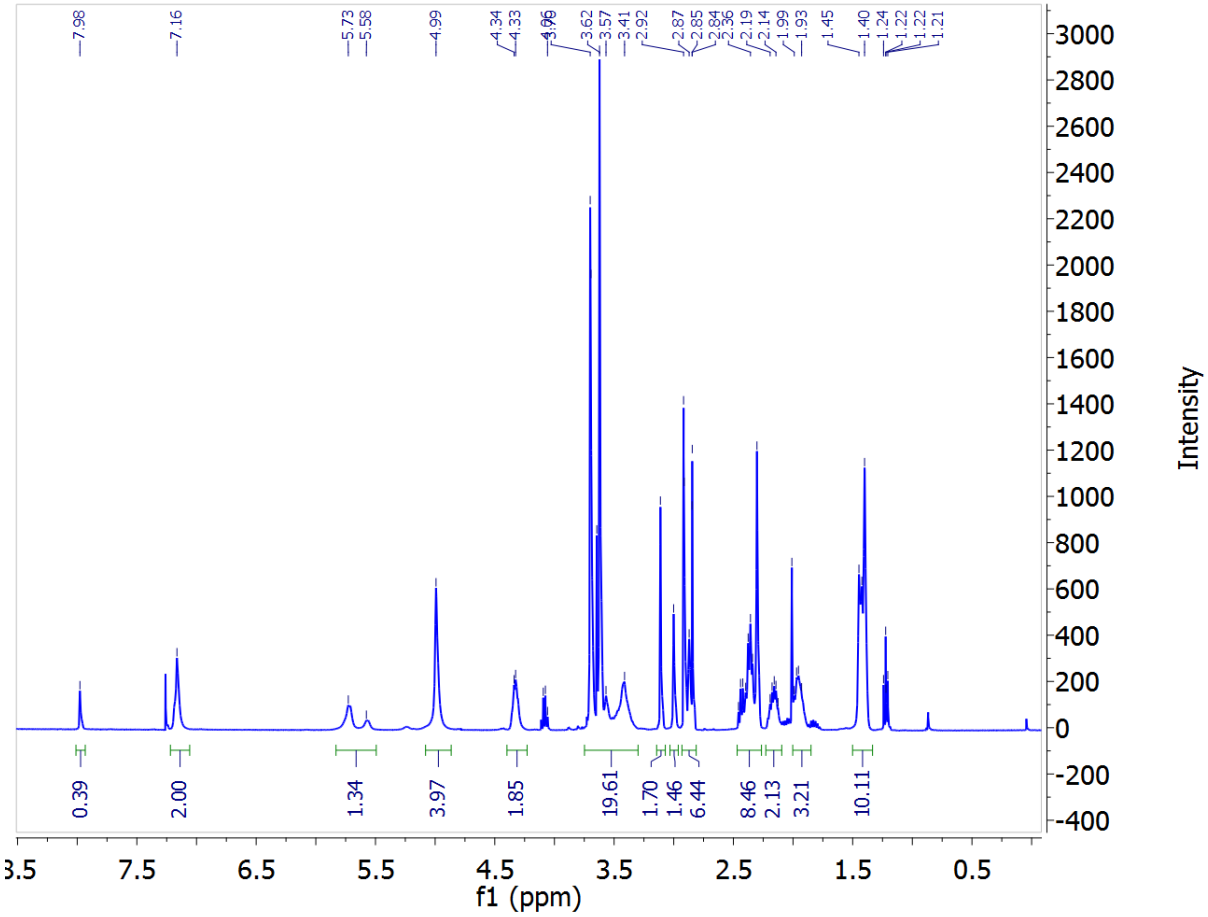
Compound 2. ^{13}C NMR ($CDCl_3$, 100 MHz)



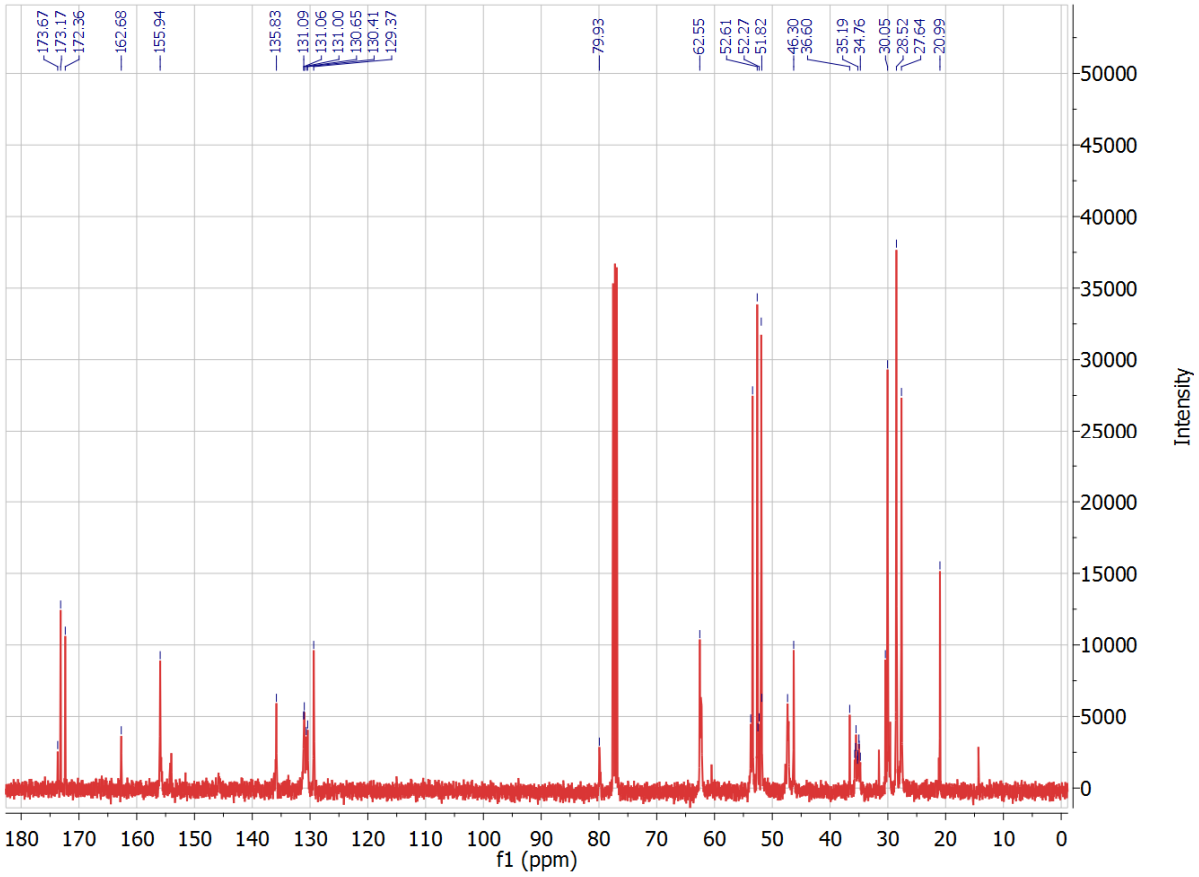
G0. ^{1}H NMR (CD_3OD, 500 MHz)



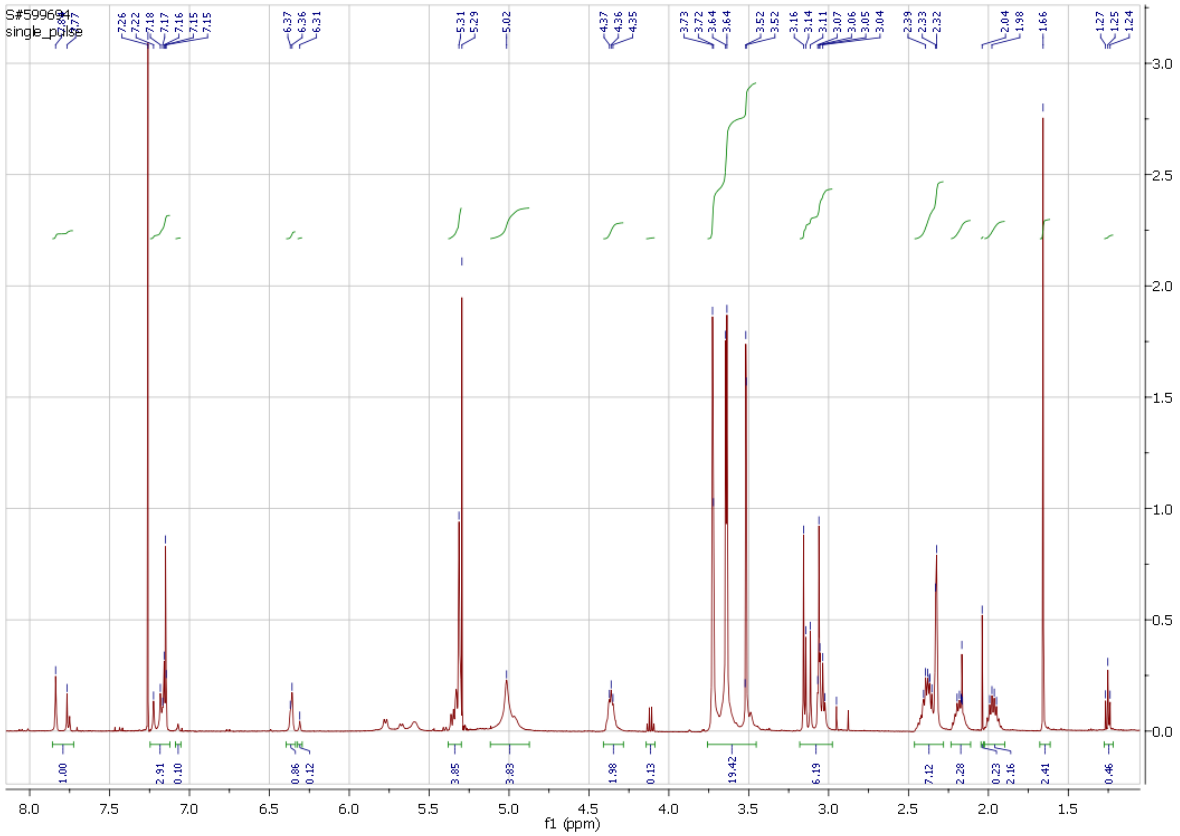
Compound 4. ^{1}H NMR (500 MHz, $CDCl_3$)



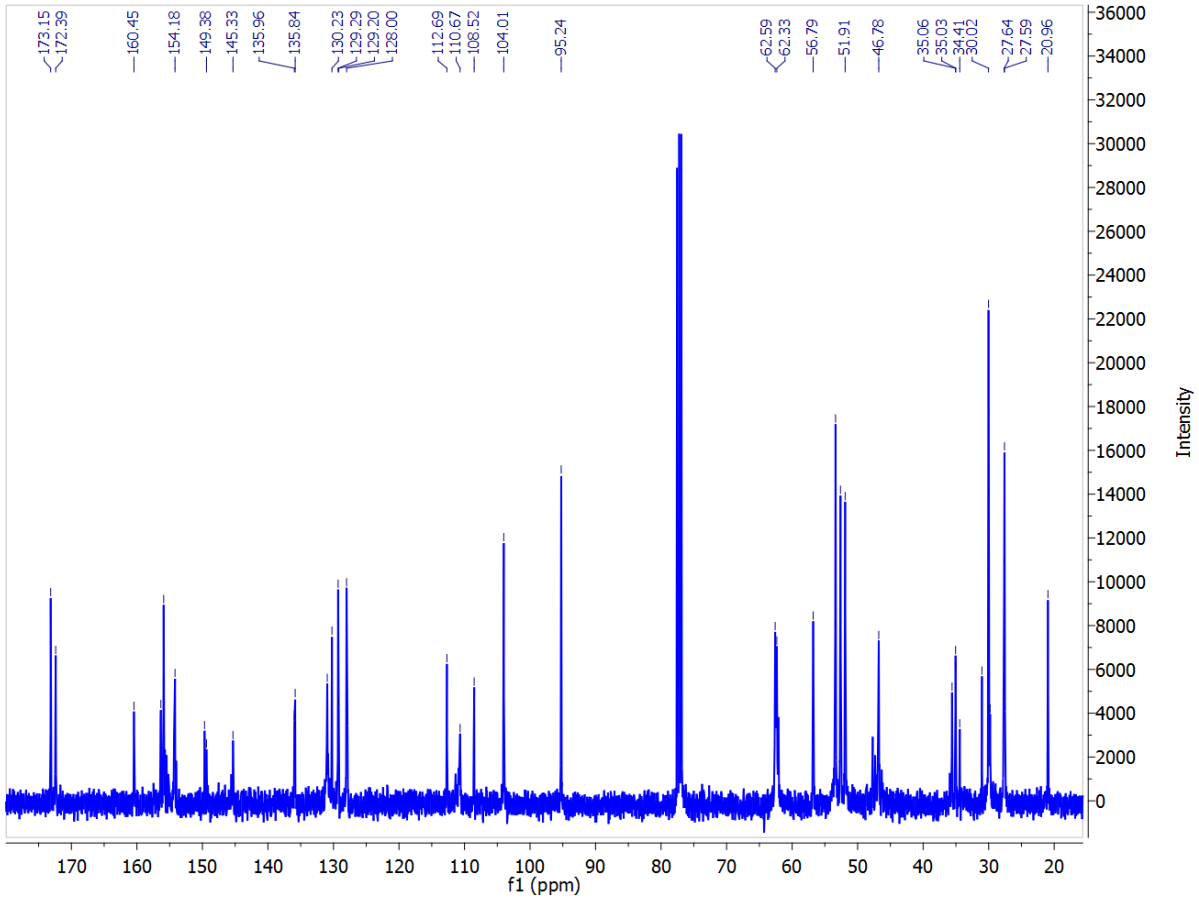
Compound 4. ^{13}C NMR (100 MHz, $CDCl_3$)



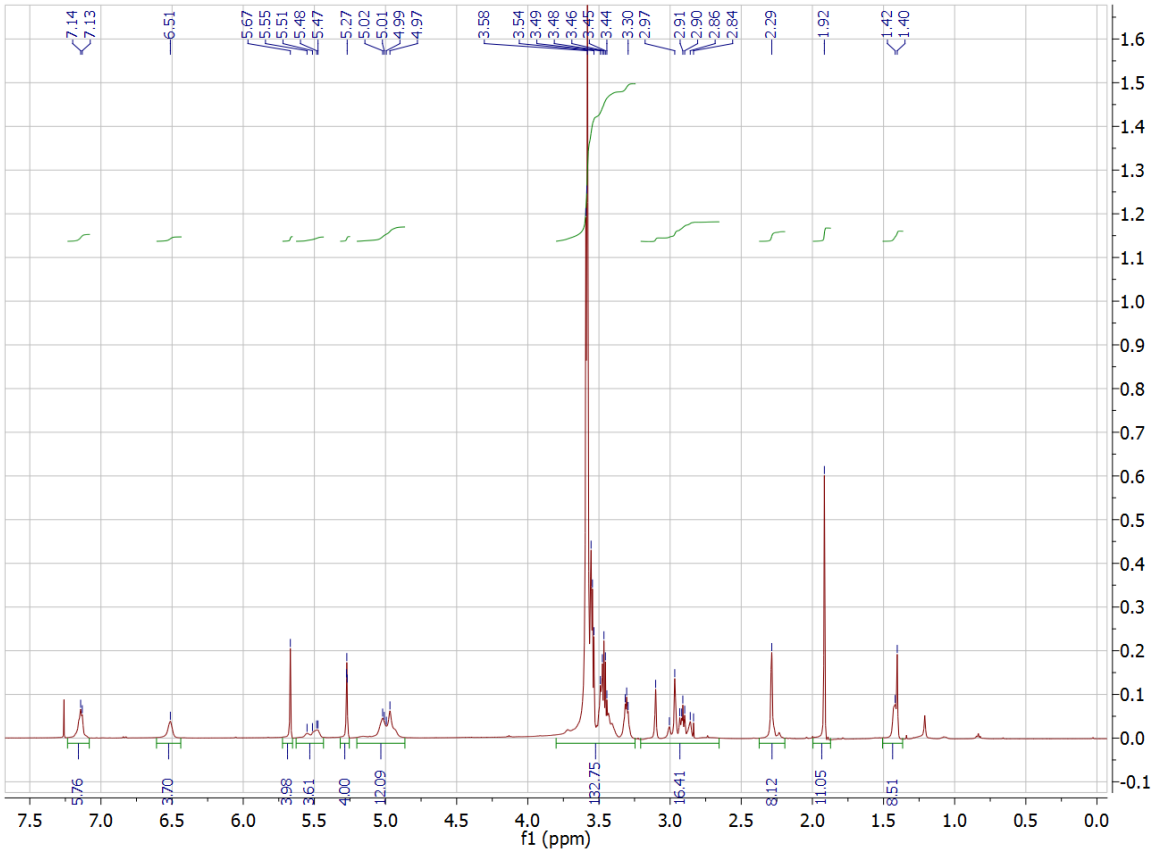
Compound 5. ^{1}H NMR (500 MHz, $CDCl_3$)



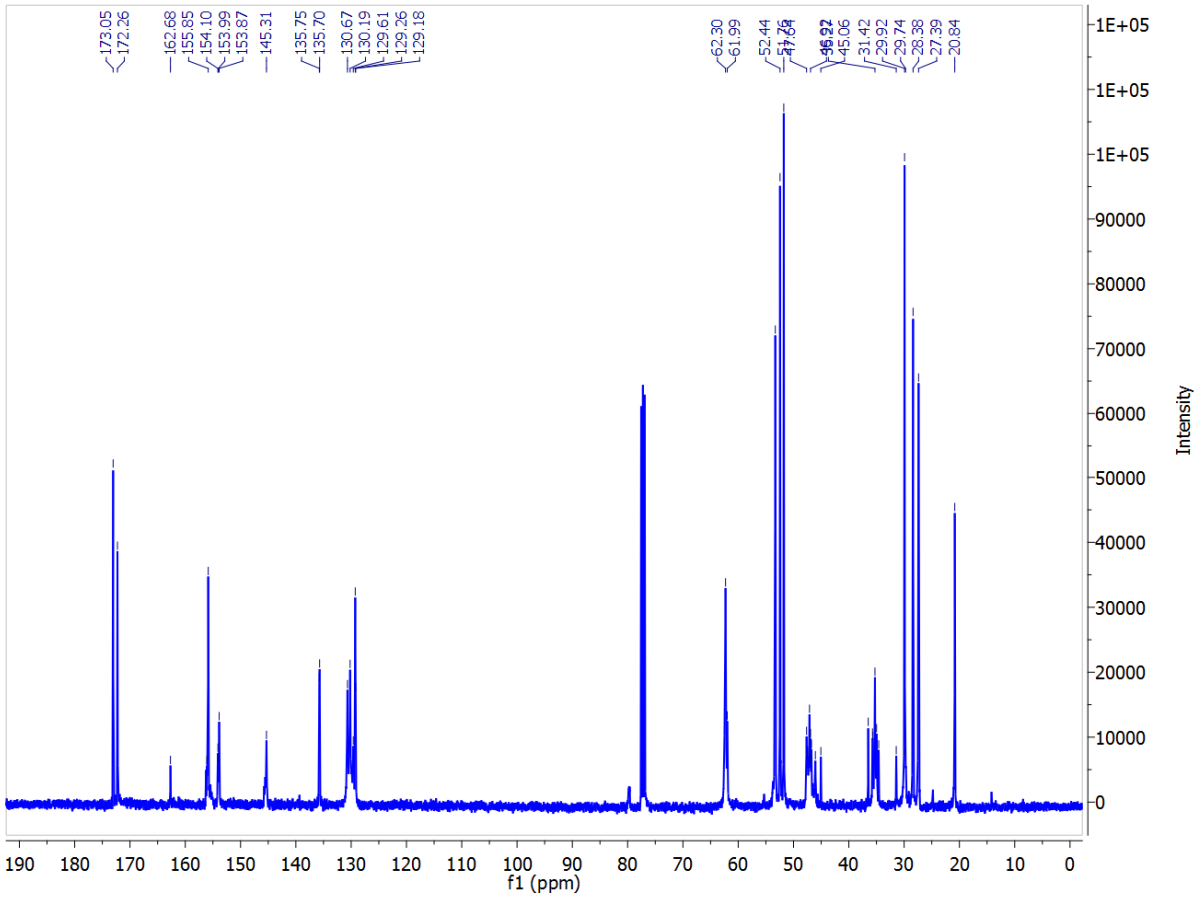
Compound 5. ^{13}C NMR (100 MHz, $CDCl_3$)



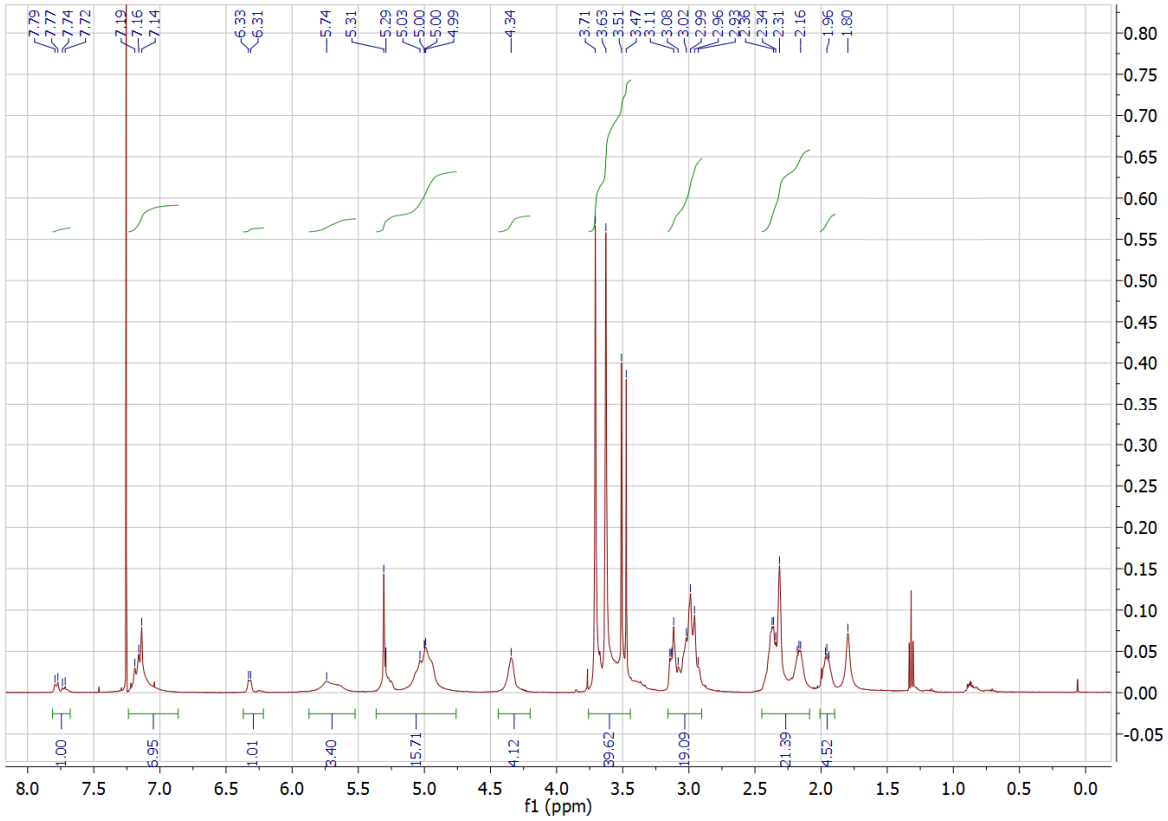
Compound 6. ^{1}H NMR (500 MHz, $CDCl_3$)



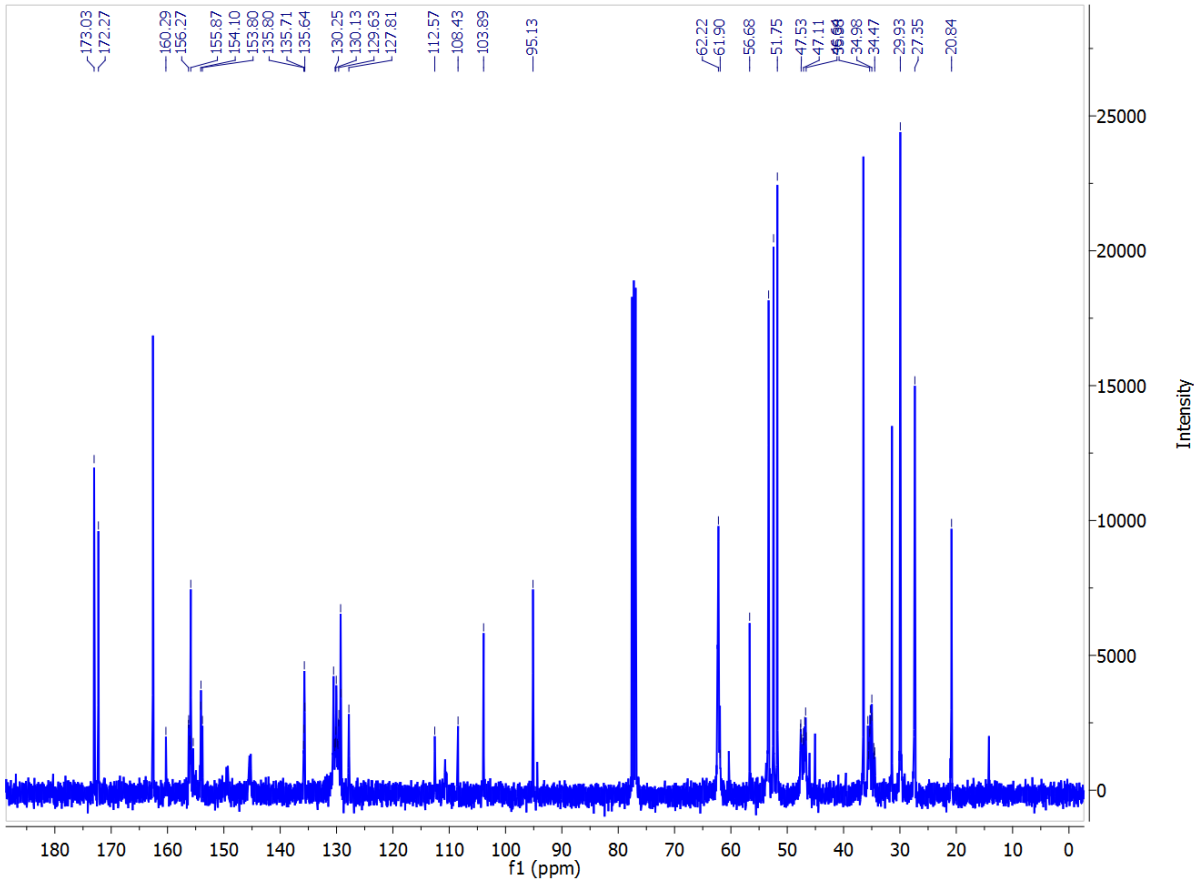
Compound 6. ^{13}C NMR (100 MHz, $CDCl_3$)



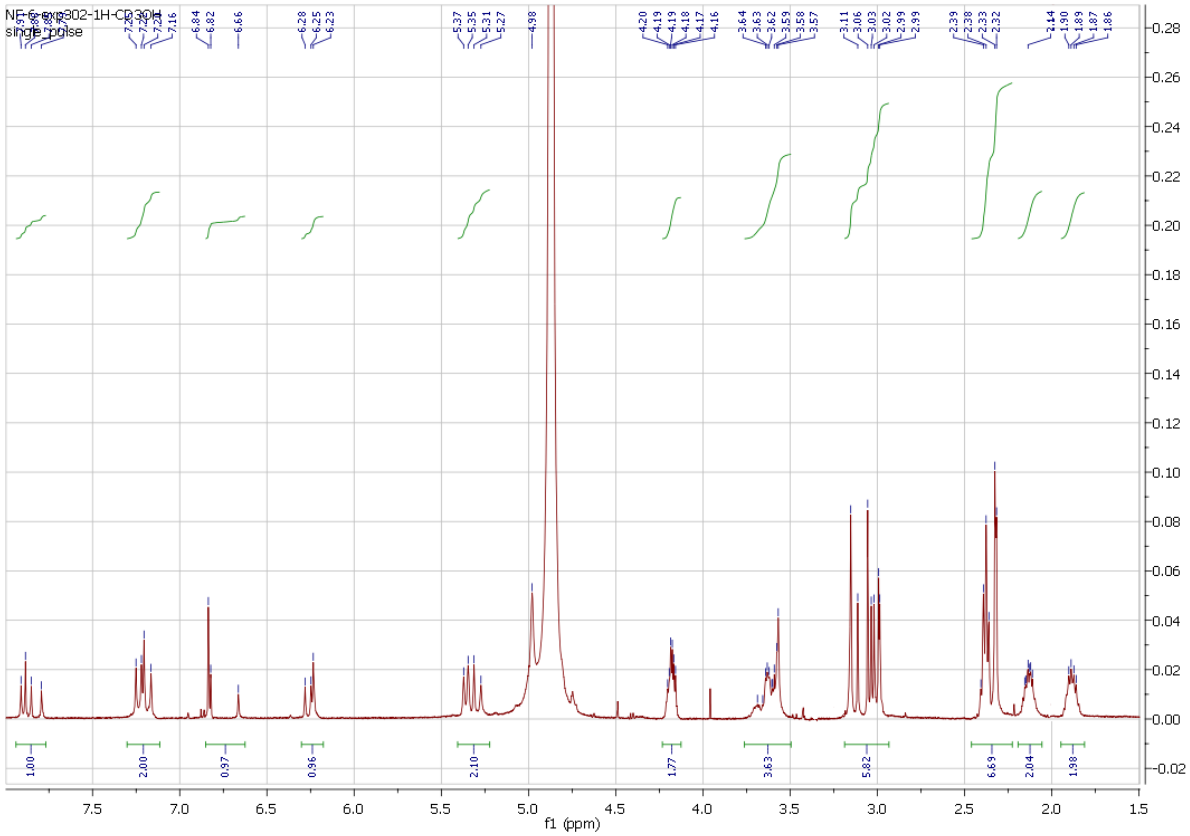
Compound 7. ^{1}H NMR (500 MHz, $CDCl_3$)



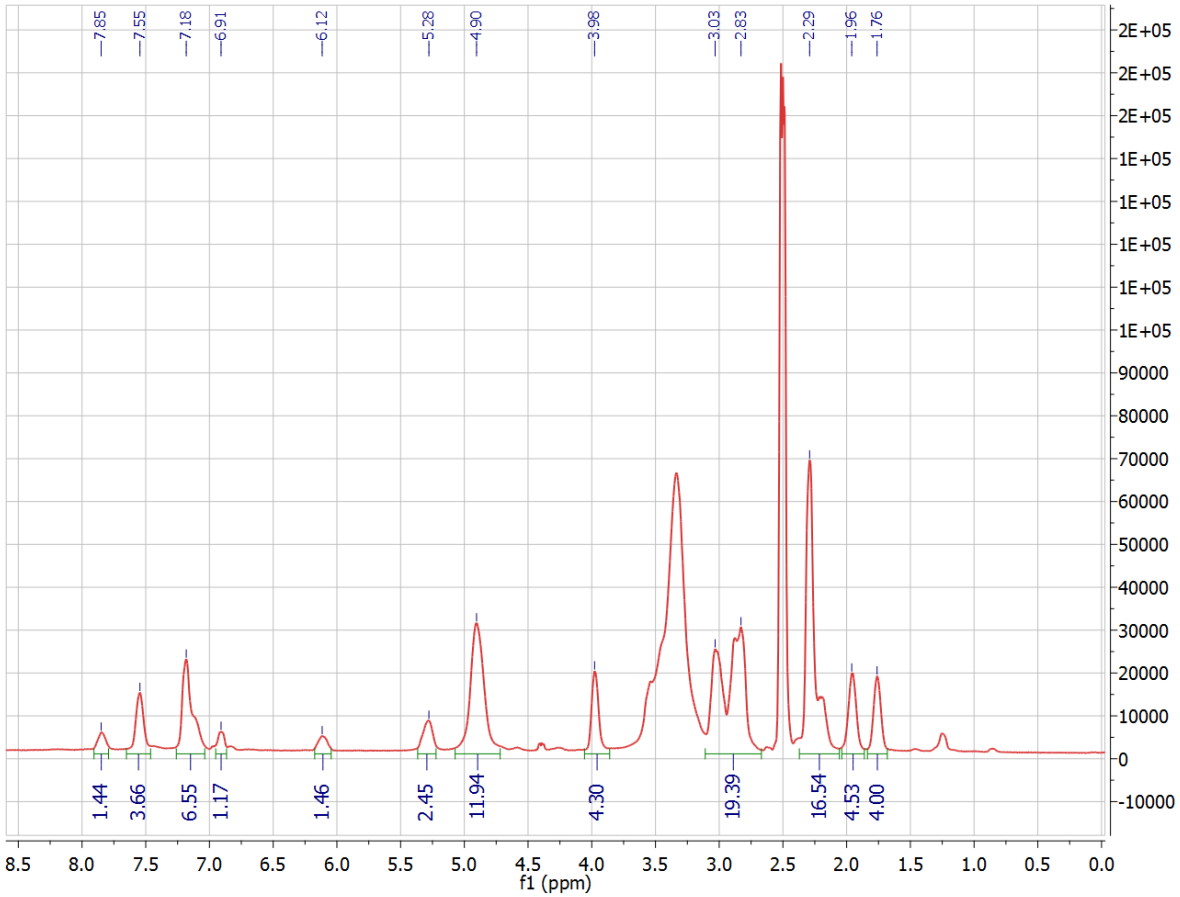
Compound 7. ^{13}C NMR (100 MHz, $CDCl_3$)



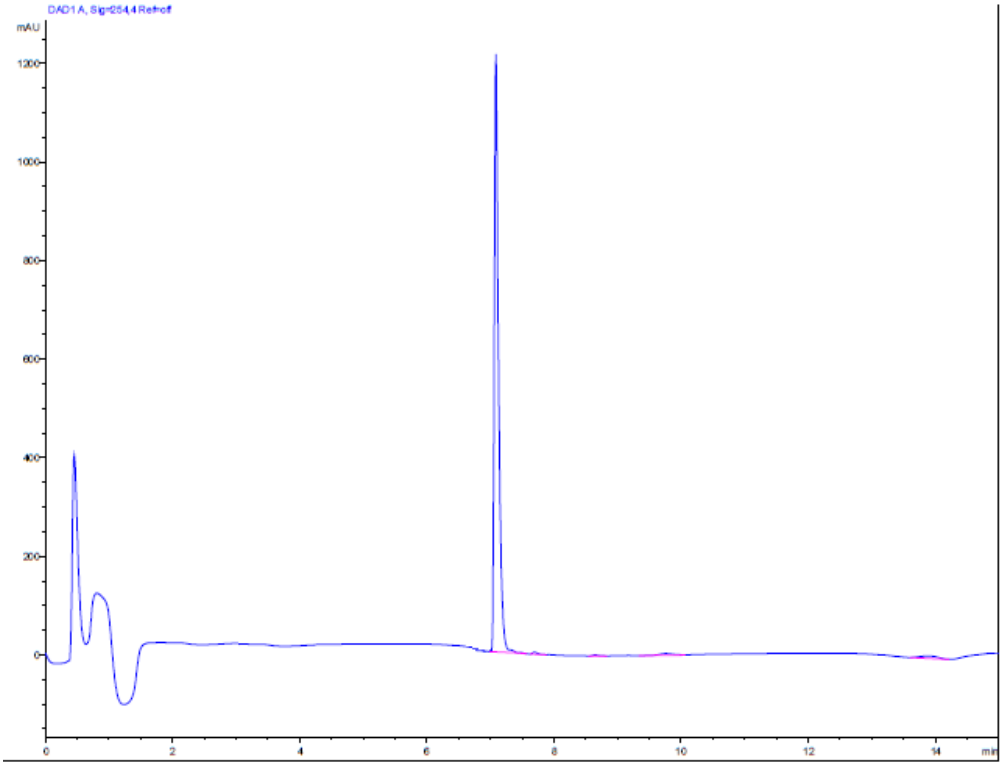
G1. ^{1}H NMR (500 MHz, CD_3OD)



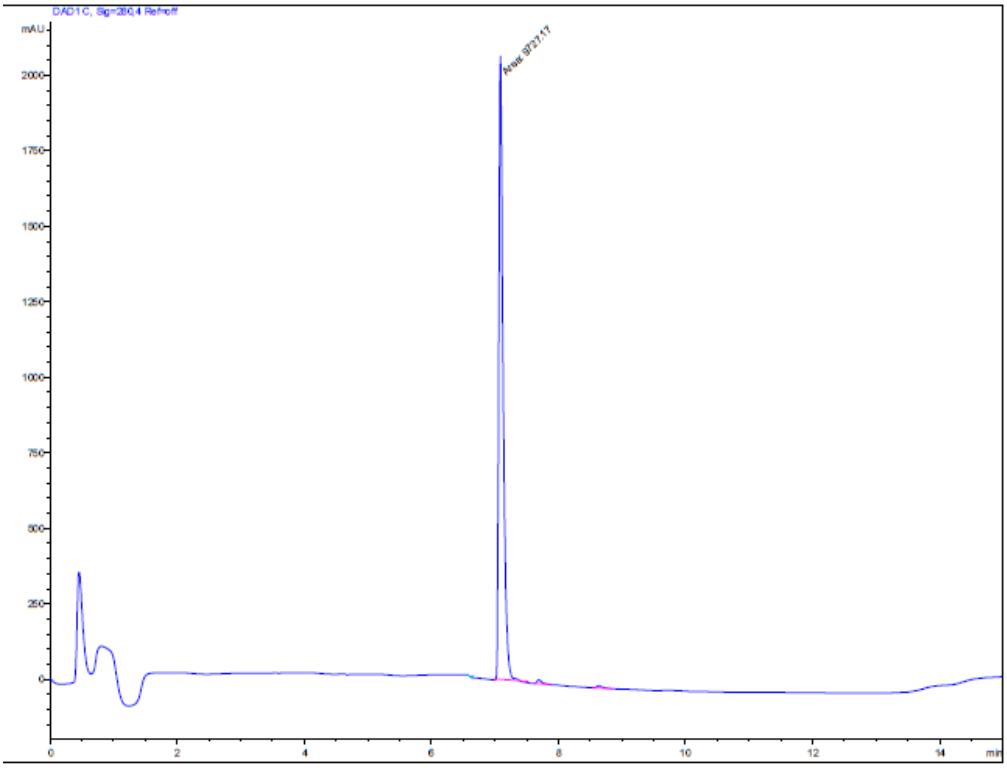
G2. ^{1}H NMR (500 MHz, DMSO$_{-d6}$)



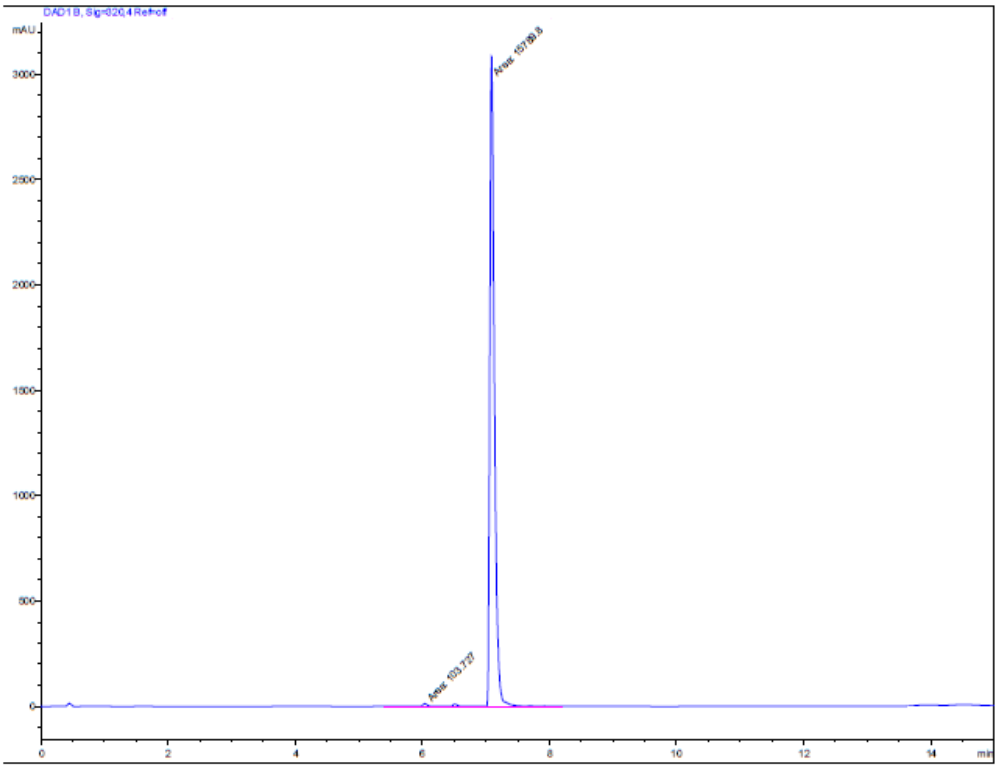
Compound 2. HPLC trace (254 nm)



Compound 2. HPLC trace (280 nm)



Compound 2. HPLC trace (320 nm)



Compound 2. Integration of HPLC traces

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=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.087 BV R  0.0683 5638.49756 1212.57092  96.7723
   2   7.477 BB    0.0634    4.34185    1.06939   0.0745
   3   7.694 BB    0.0795   22.44258    4.26079   0.3852
   4   8.642 BB    0.1061   11.29974    1.64536   0.1939
   5   9.764 BV    0.2621   56.17157    3.34252   0.9641
   6  13.880 BB    0.3094   93.81101    4.94236   1.6101

Totals :                  5826.56432 1227.83134


Signal 2: DAD1 B, Sig=320,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.039 FM    0.1230  103.72677   14.05689   0.6488
   2   6.519 VV    0.1277   92.96394   11.32828   0.5815
   3   7.091 MF    0.0830 1.57898e4  3169.99609  98.7696

Totals :                  1.59865e4  3195.38127


Signal 3: DAD1 C, Sig=280,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.088 MM    0.0765 9727.17480 2119.04028  98.8601
   2   7.690 VV b  0.0947   66.47274   12.35918   0.6756
   3   8.642 BB    0.1045   45.68644    7.34858   0.4643

Totals :                  9839.33399 2138.74805
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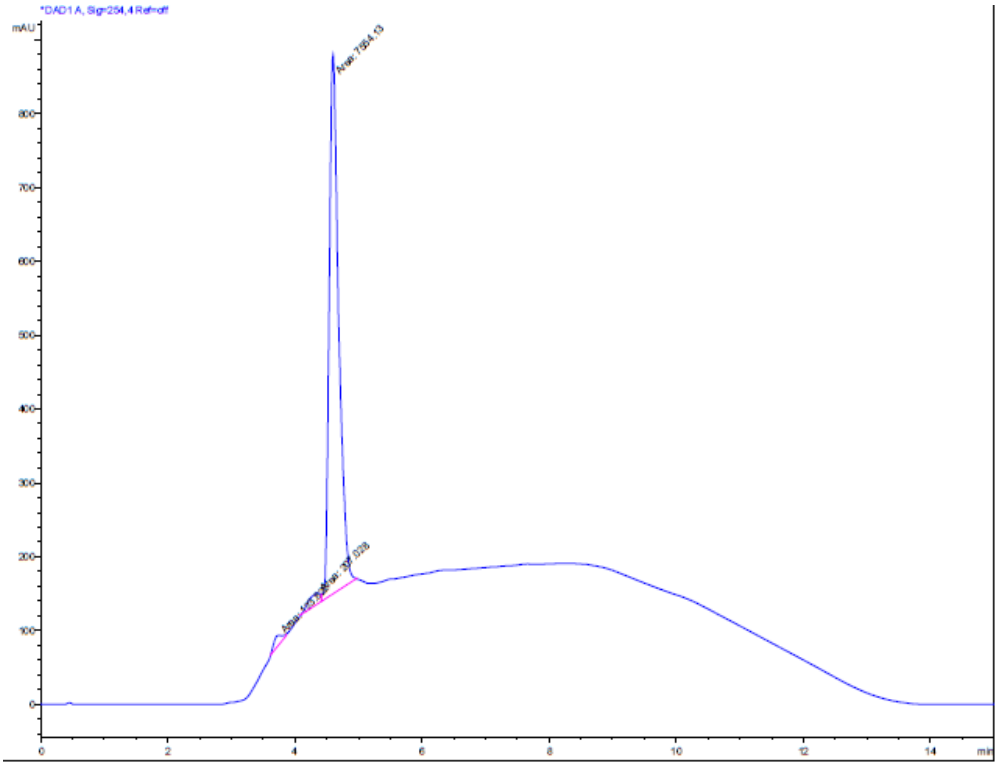
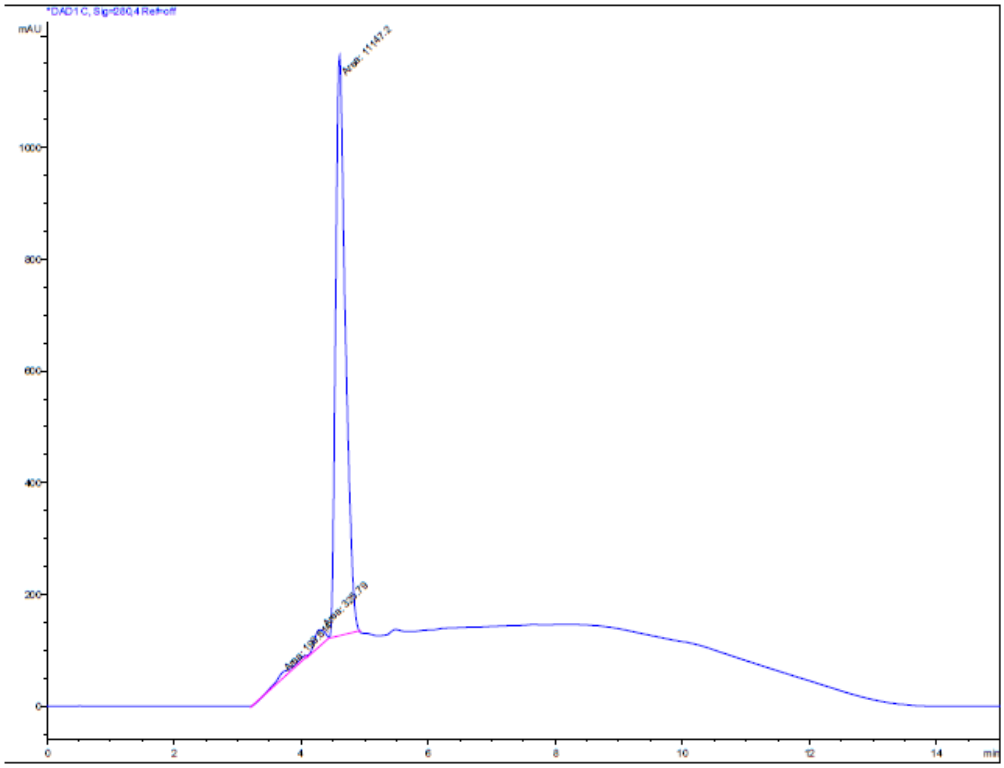
Comound 4. HPLC trace (254 nm)



Compound 4. HPLC trace (280 nm)



Compound 4. Integration of HPLC traces.

Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

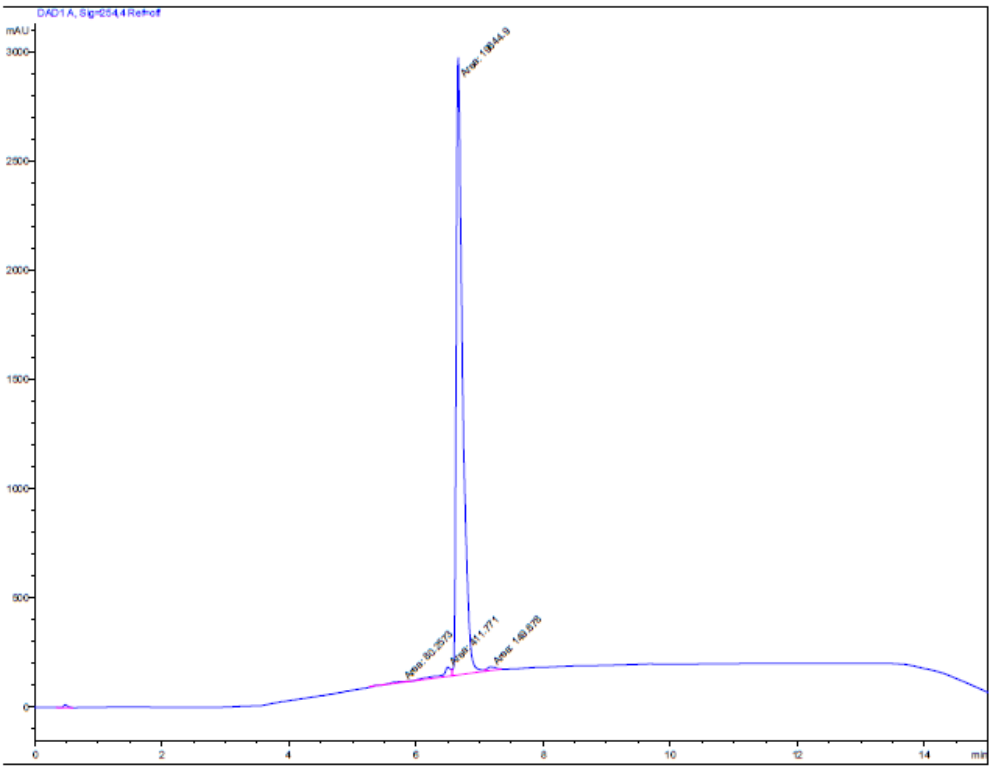
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.742	MM	0.1510	123.82155	13.66807	1.5703
2	4.361	MF	0.2372	207.02815	14.54572	2.6256
3	4.601	FM	0.1724	7554.13379	730.36456	95.8041
Totals :				7884.98349	758.57836	

Signal 2: DAD1 C, Sig=280,4 Ref=off

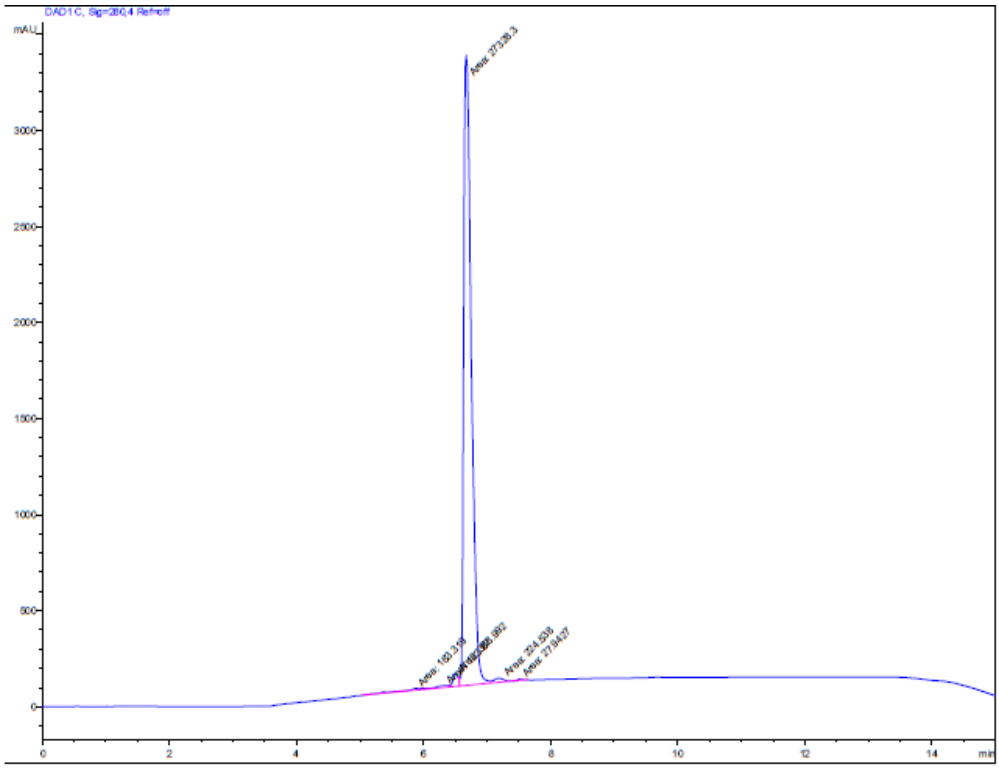
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.693	MM	0.3133	199.61351	10.61742	1.7101
2	4.304	MM	0.1850	325.79041	29.34939	2.7911
3	4.606	MM	0.1783	1.11472e4	1041.94250	95.4988
Totals :				1.16726e4	1081.90932	

*** End of Report ***

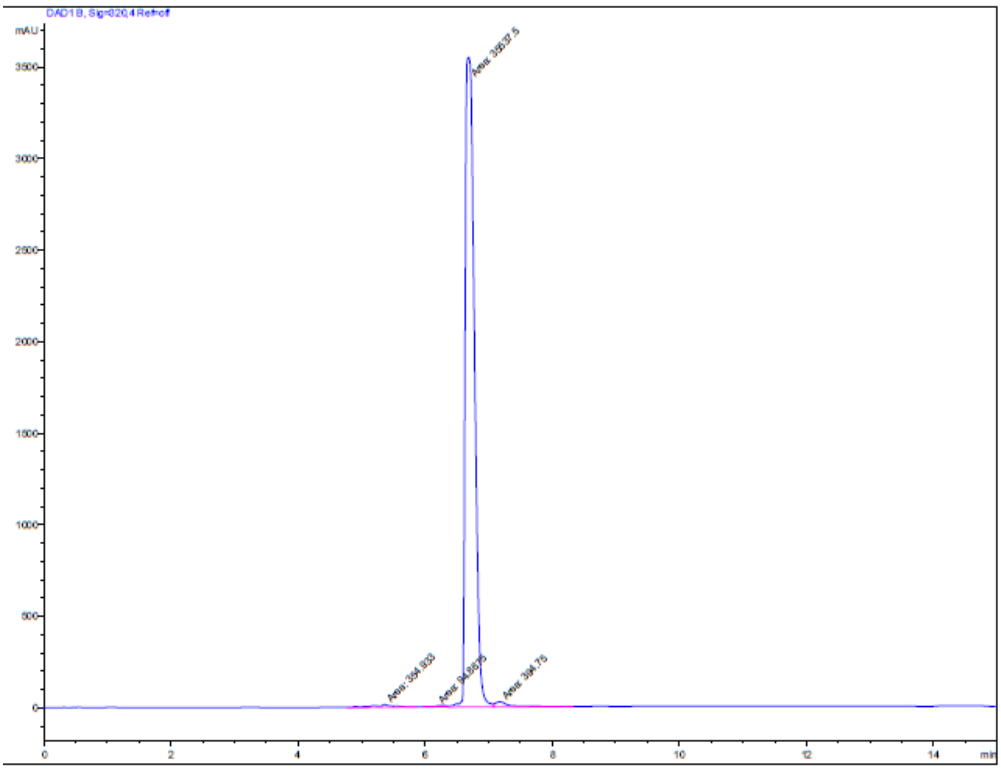
Compound 5. HPLC trace (254 nm)



Coumpound 5. HPLC trace (280 nm)



Compound 5. HPLC trace (320 nm)



Compound 5. Integration of HPLC traces.

Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	0.483	VB	0.0729	65.35059	12.94502	0.3211
2	5.777	MF	0.4038	80.25726	3.31254	0.3943
3	6.500	FM	0.1687	411.77136	40.68394	2.0232
4	6.666	FM	0.1157	1.96449e4	2829.31128	96.5259
5	7.176	FM	0.1469	149.67824	16.97940	0.7354
Totals :				2.03520e4	2903.23219	

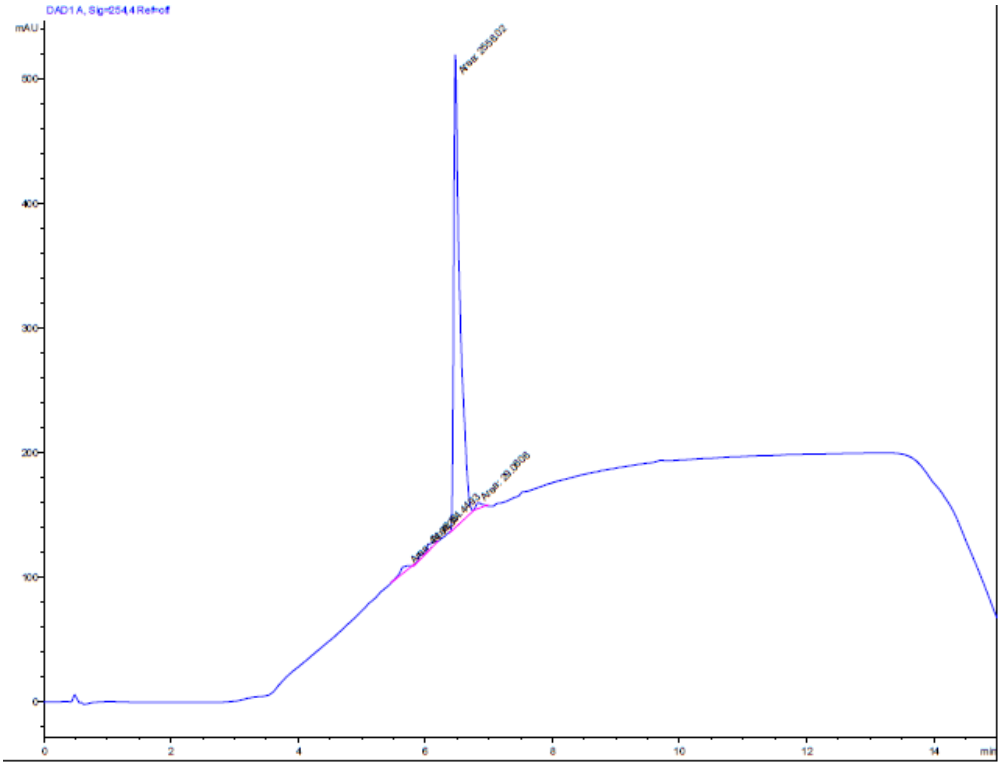
Signal 2: DAD1 B, Sig=320,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.360	MM	0.3675	354.93338	16.09779	0.9756
2	6.167	MF	0.2190	94.86752	7.22114	0.2608
3	6.681	FM	0.1661	3.55375e4	3566.51978	97.6787
4	7.173	FM	0.2498	394.75034	26.33272	1.0850
Totals :				3.63820e4	3616.17143	

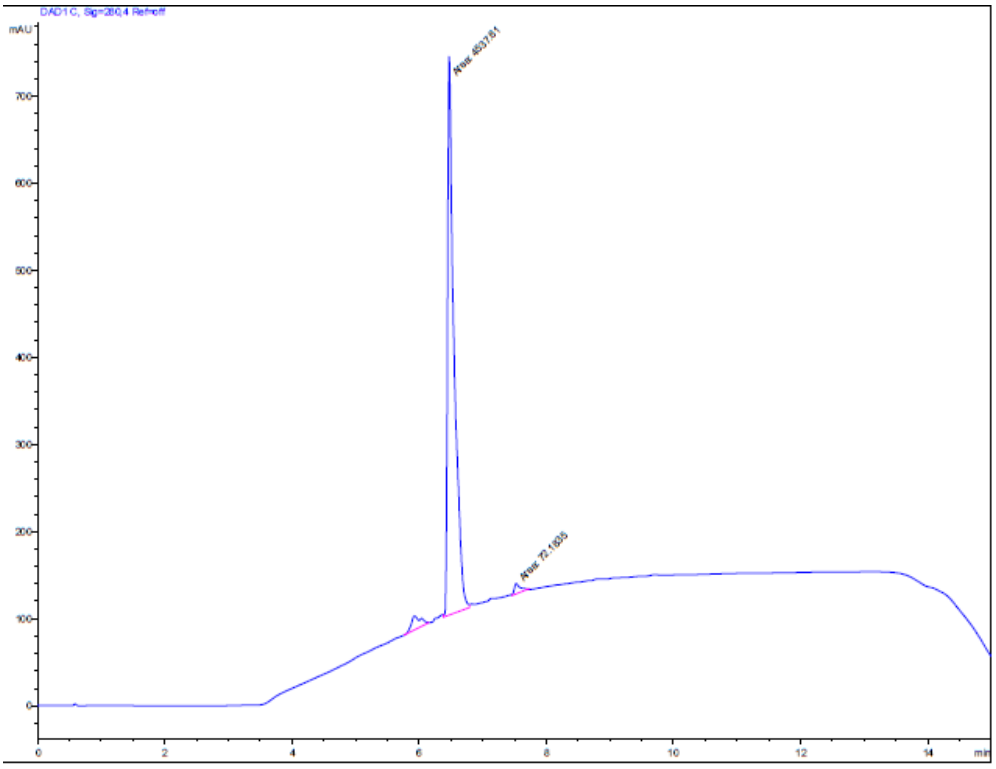
Signal 3: DAD1 C, Sig=280,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.877	MF	0.3279	163.31876	8.30139	0.5780
2	6.325	FM	0.2284	123.86954	9.03941	0.4384
3	6.503	FM	0.0979	388.99210	66.23907	1.3766
4	6.677	FM	0.1349	2.73283e4	3375.37354	96.7135
5	7.239	MF	0.1814	224.53767	20.63080	0.7946
6	7.517	FM	0.0600	27.94269	7.76740	0.0989
Totals :				2.82570e4	3487.35160	

Compound 6. HPLC trace (254 nm)



Compound 6. HPLC trace (280 nm)



Compound 6. Integration of HPLC traces.

Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.727	MM	0.1874	44.76364	3.02000	1.6676
2	6.047	MM	0.1731	54.44934	5.24206	2.0284
3	6.475	MM	0.1118	2556.02197	381.11389	95.2213
4	6.838	MM	0.1037	29.06061	4.66866	1.0826

Totals : 2684.29557 394.04461

Signal 2: DAD1 B, Sig=320,4 Ref=off

Signal 3: DAD1 C, Sig=280,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.967	BB	0.2055	156.09244	12.87076	3.2752
2	6.477	MM	0.1139	4537.61133	664.23846	95.2102
3	7.530	MM	0.0960	72.18346	12.52650	1.5146

Totals : 4765.88722 689.63572

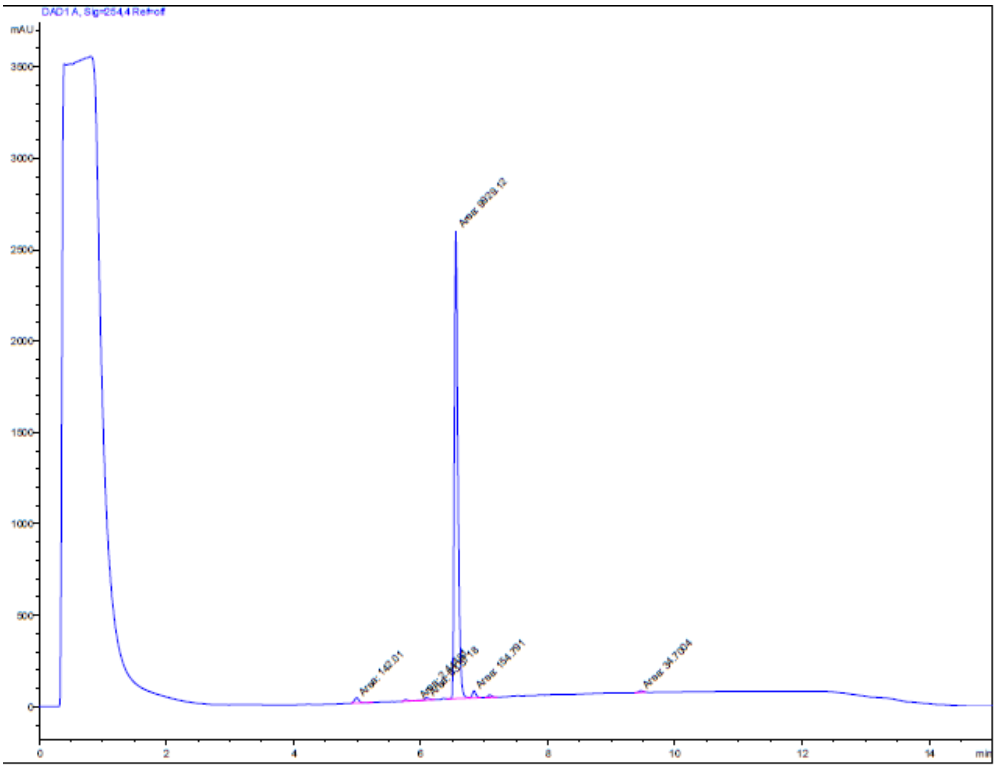
Signal 4: MSD1 TIC, MS File

Peak #	RetTime [min]	Type	Width [min]	Area	Height	Area %
1	6.566	BB	0.2446	5.07602e6	2.73966e5	100.0000

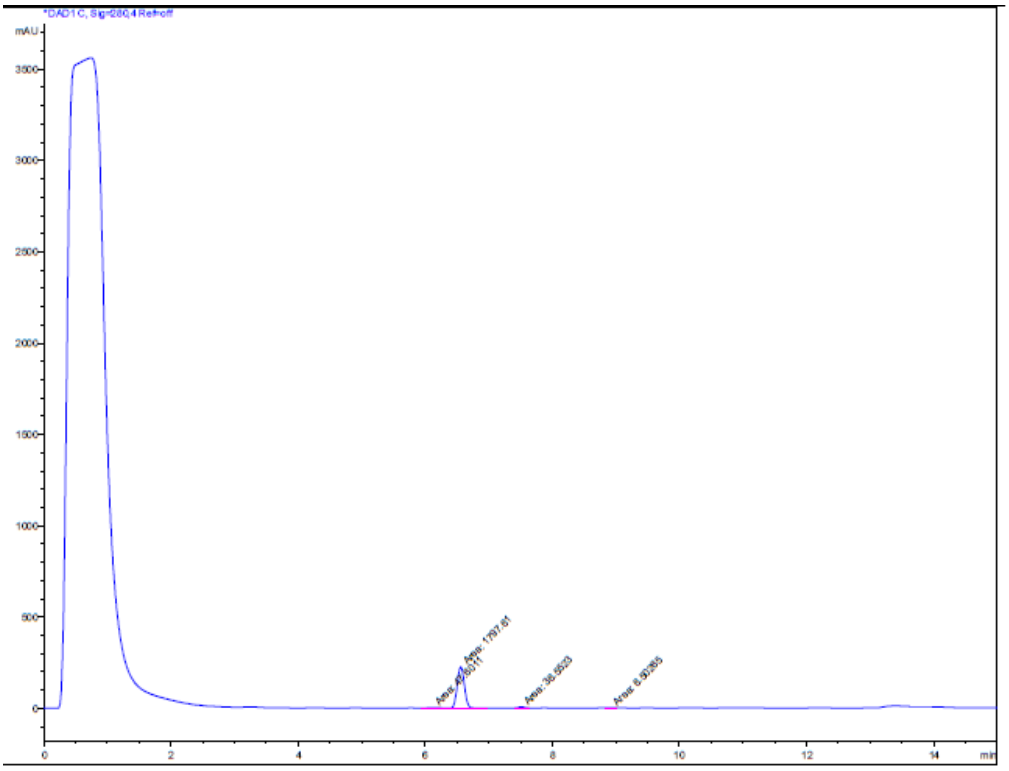
Totals : 5.07602e6 2.73966e5

*** End of Report ***

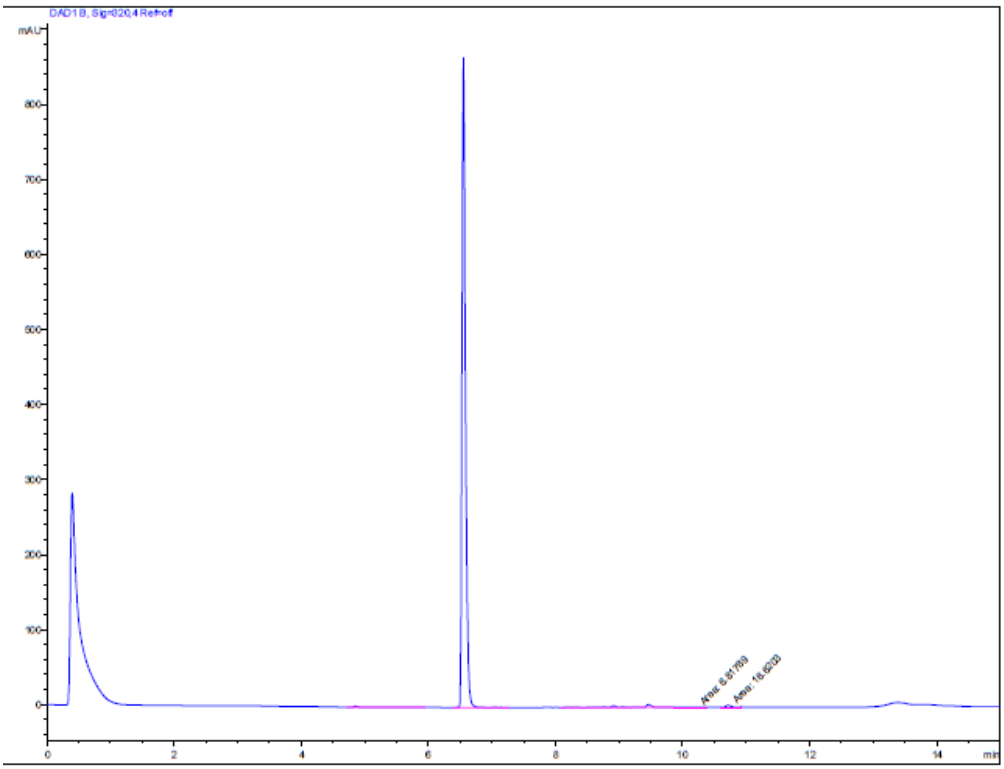
Compound 7. HPLC trace (254 nm)



Compound 7. HPLC trace (280 nm)



Compound 7. HPLC trace (320 nm)



Compound 7. Integration of HPLC traces.

Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.995	FM	0.0795	142.01025	29.76386	1.3629
2	5.212	BV	0.0551	3.91492	1.11138	0.0376
3	5.766	BB	0.0569	33.42433	8.67672	0.3208
4	5.945	MF T	0.0773	2.44491	5.27159e-1	0.0235
5	6.095	FM T	0.0789	63.57177	13.42993	0.6101
6	6.554	MF	0.0645	9929.12207	2566.26416	95.2911
7	6.840	FM	0.0647	154.79086	39.89325	1.4855
8	7.086	BB	0.0572	55.79729	14.40436	0.5355
9	9.465	MM	0.0630	34.70042	9.17674	0.3330
Totals :				1.04198e4	2683.24757	

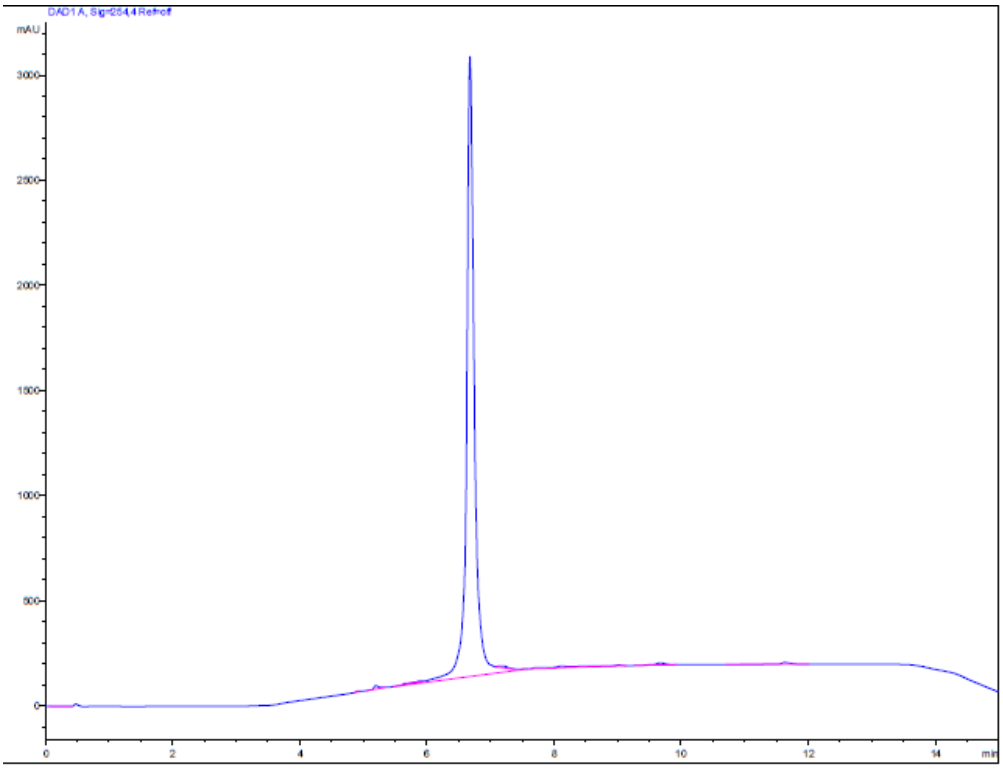
Signal 2: DAD1 B, Sig=320,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.866	BV	0.2177	22.28537	1.40016	0.6595
2	6.559	BB	0.0885	3280.91870	677.80762	97.0903
3	8.921	VV	0.1580	25.80622	2.38902	0.7637
4	9.474	VV	0.1189	26.79691	3.96449	0.7930
5	10.230	MF	0.2962	6.81789	3.83645e-1	0.2018
6	10.754	MF	0.0959	16.62031	2.88862	0.4918
Totals :				3379.24540	688.83354	

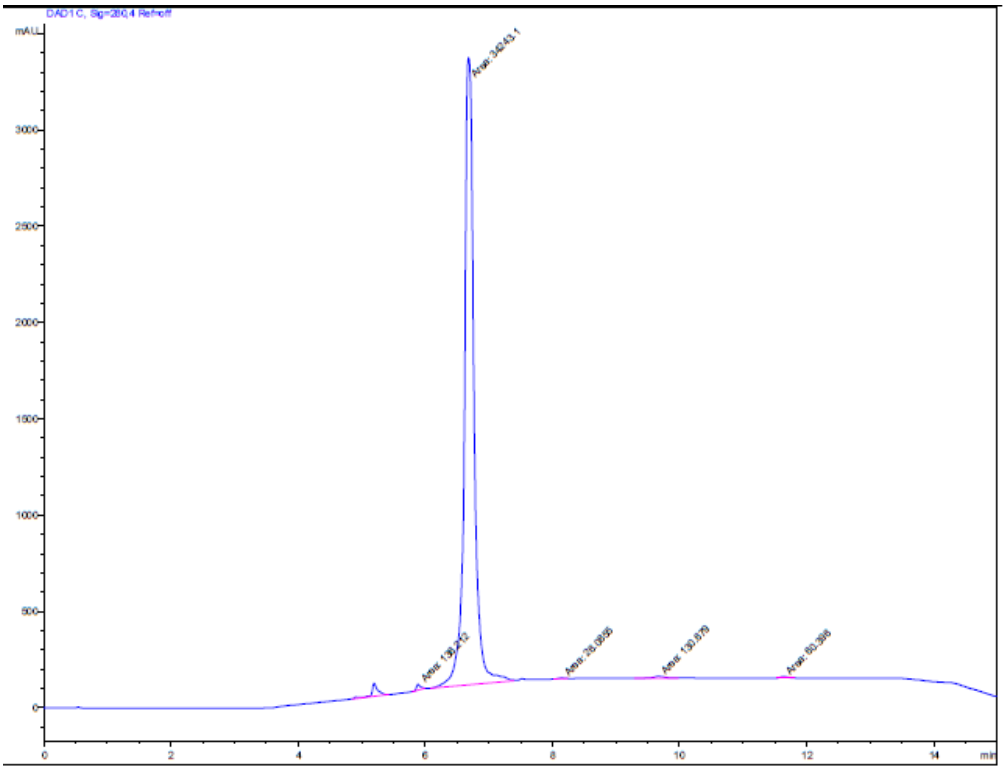
Signal 3: DAD1 C, Sig=280,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.113	MM	0.1756	47.60110	4.51731	2.5209
2	6.560	MM	0.1314	1797.60681	228.07796	95.1990
3	7.517	MM	0.1100	36.55231	5.53989	1.9358
4	8.924	MM	0.0874	6.50265	1.24025	0.3444
Totals :				1888.26287	239.37542	

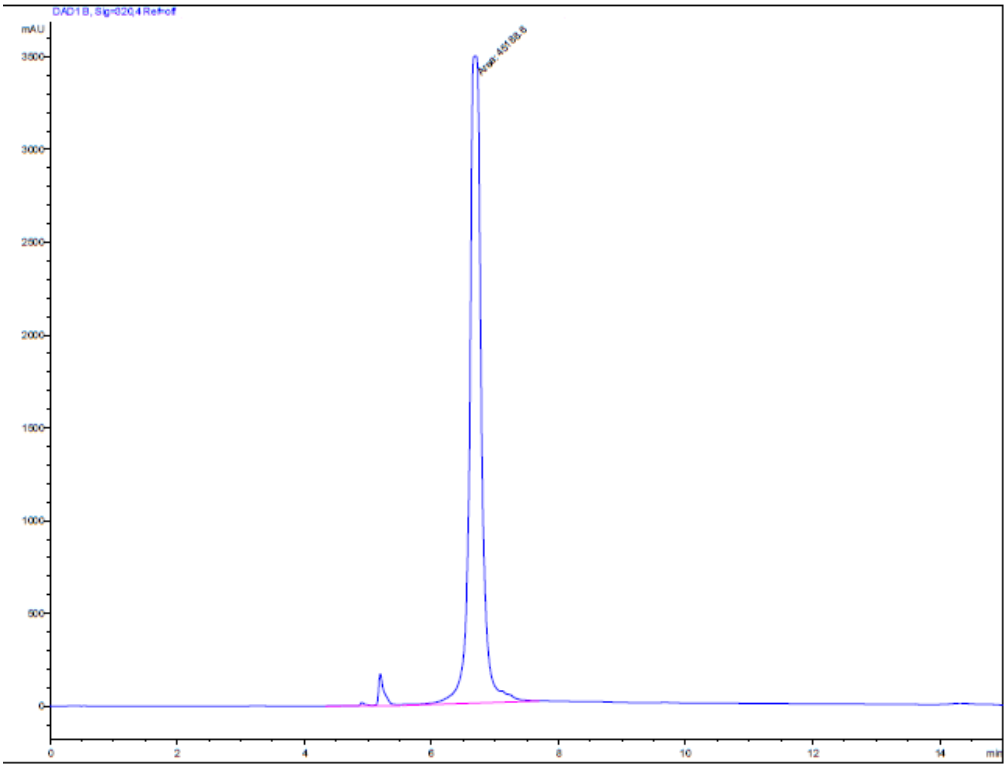
G1. HPLC trace (254 nm)



G1. HPLC trace (280 nm)



G1. HPLC trace (320 nm)



G1. Integration of HPLC traces.

Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	0.313	BV	0.1686	18.37831	1.36913	0.0703
2	4.915	BB	0.0511	11.90346	3.73861	0.0455
3	5.198	BB	0.0741	91.52818	17.75304	0.3502
4	5.660	BV T	0.0535	14.56638	4.30759	0.0557
5	5.891	VV T	0.0927	20.83250	3.08836	0.0797
6	6.679	VV R	0.1265	2.54079e4	2949.79663	97.2127
7	7.182	VV T	0.1476	82.89394	8.51596	0.3172
8	7.725	BV	0.1011	29.98930	4.42265	0.1147
9	7.890	VV	0.0906	23.02784	3.50618	0.0881
10	8.131	VV	0.2017	96.51692	6.71503	0.3693
11	8.548	VV	0.2108	54.76419	3.21435	0.2095
12	9.013	VB	0.2111	67.22124	4.14828	0.2572
13	9.673	BV	0.1715	131.66780	10.55944	0.5038
14	11.634	BB	0.1405	85.21042	8.68275	0.3260
Totals :				2.61364e4	3029.81800	

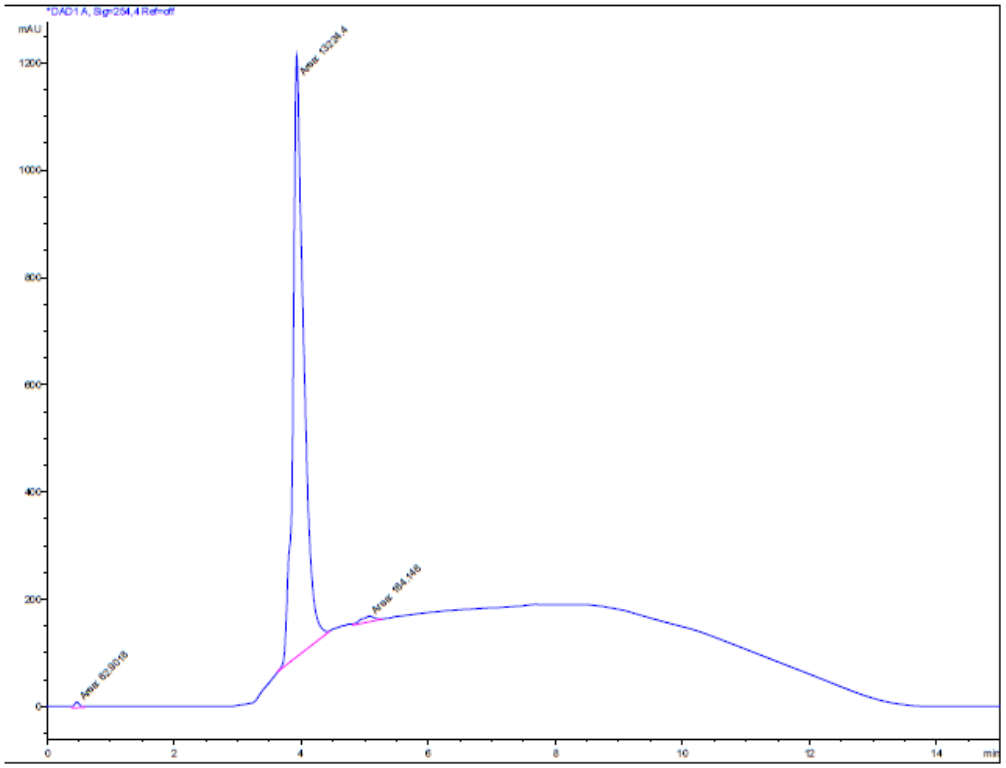
Signal 2: DAD1 B, Sig=320,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.436	BB	0.1192	9.24432	1.36189	0.0199
2	4.926	BV	0.1049	110.15494	17.62743	0.2373
3	5.215	VV	0.1234	1106.07068	154.75166	2.3830
4	6.686	MM	0.2159	4.51886e4	3488.65259	97.3597
Totals :				4.64141e4	3662.39358	

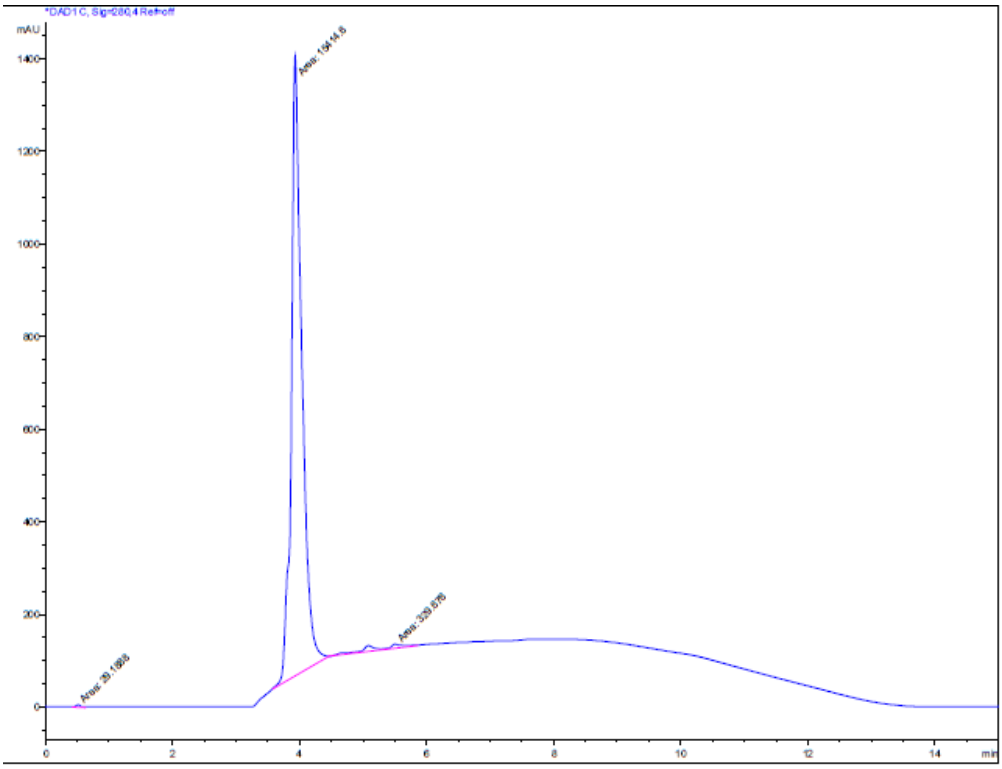
Signal 3: DAD1 C, Sig=280,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.217	BB	0.1277	449.18762	59.75112	1.2817
2	5.891	MM	0.0695	136.21172	32.66082	0.3887
3	6.685	MM	0.1719	3.42431e4	3320.40356	97.7100
4	8.152	MM	0.0940	26.08551	4.62395	0.0744
5	9.671	MM	0.2180	130.67891	9.99114	0.3729
6	11.637	MM	0.1353	60.39601	7.44215	0.1723
Totals :				3.50457e4	3434.87274	

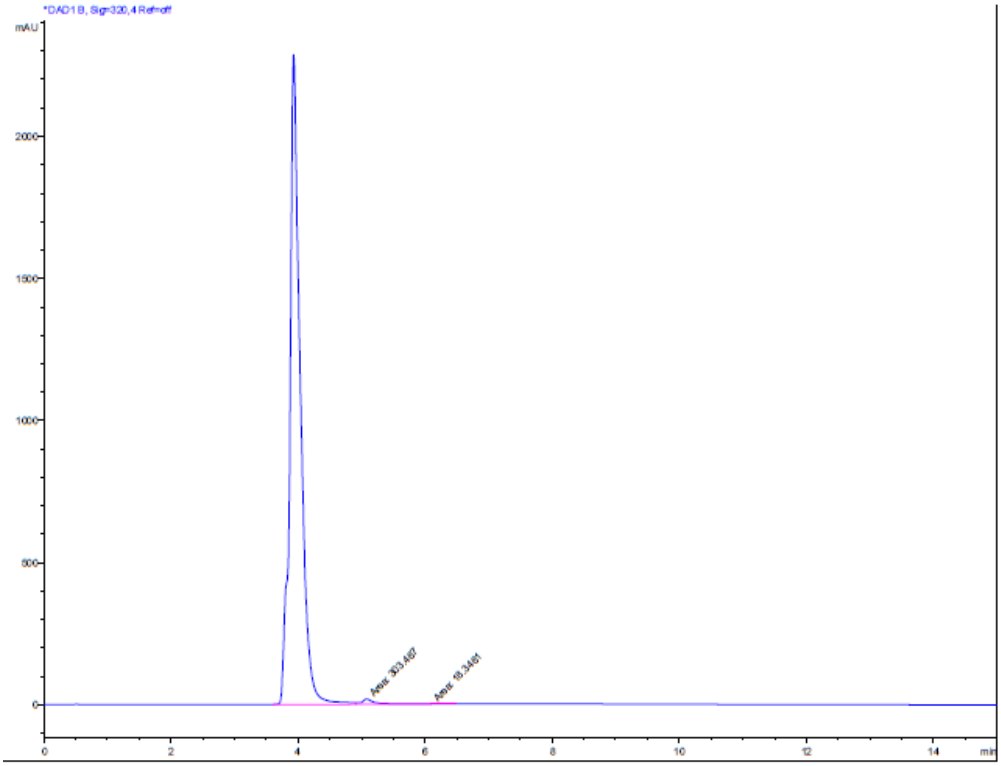
G2. HPLC trace (254 nm)



G2. HPLC trace (280 nm)



G2. HPLC trace (320 nm)

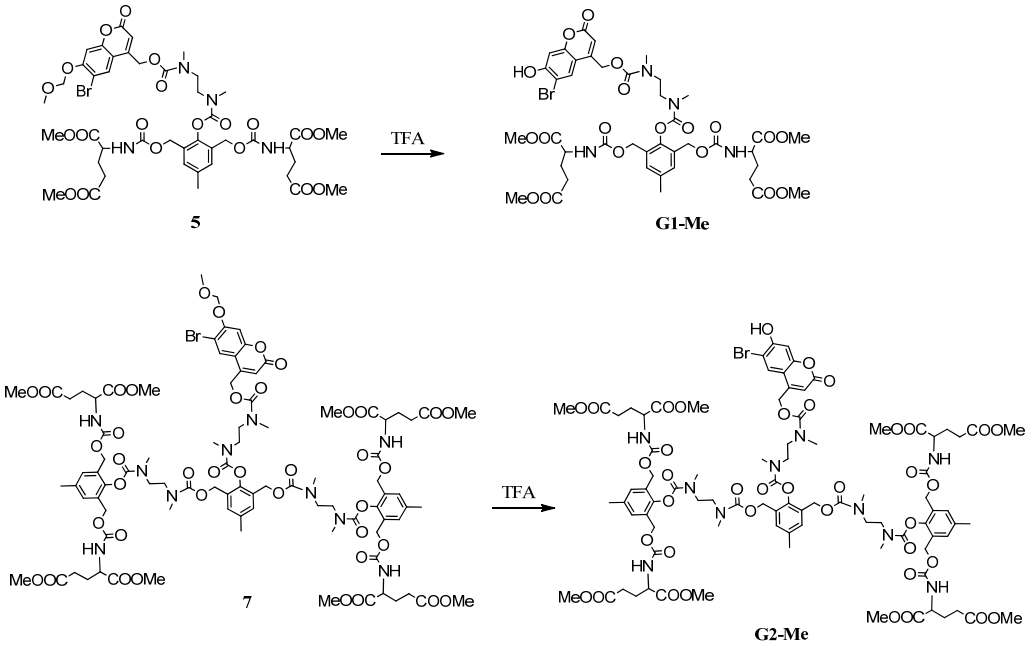


G2. Integration of HPLC traces.

```
================================================================
                      Area Percent Report
================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.472 MM    0.1004   62.90178   10.44576   0.4676
   2   3.932 MM    0.1966 1.32244e4  1121.18335  98.3121
   3   5.078 MM    0.2512  164.14577   10.89043   1.2203

Totals :                  1.34514e4  1142.51954


Signal 2: DAD1 B, Sig=320,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   3.949 BV    0.1935 2.60469e4  2089.13403  98.7796
   2   5.081 MF    0.2641  303.46747   19.15088   1.1509
   3   6.088 FM    0.2384   18.34607    1.00418   0.0696

Totals :                  2.63688e4  2109.28909


Signal 3: DAD1 C, Sig=280,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.515 MM    0.0925   29.18877    5.25780   0.1850
   2   3.935 MM    0.1898 1.54146e4  1353.60974  97.7249
   3   5.507 MM    0.5934  329.67557    9.25875   2.0901

Totals :                  1.57735e4  1368.12629
```

Control experiment to evaluate the influence of the byproducts of dendrimers' degradation on the Amplex Red assay:

Compounds **5** and **7** were treated with TFA in dry DCM for 30 min to remove the methoxymethyl protecting group (Scheme S1). The solvents were removed on rotary evaporator. The 1 mM solutions of **G1-Me** and **G2-Me** in acetonitrile/PBS pH 7.4 (1/2) were irradiated with NIR light for 30 min. After that, the irradiated and the non-irradiated control solutions were diluted to 3.5 μM (for **G1-Me**) and 1.75 μM (for **G2-Me**) with PBS pH 7.4 and incubated with 2 nM of *L*-glutamic acid at 37˚C for 96 hours before analysis using the Amplex Red assay. The amount of *L*-glutamic acid detected in the presence of both irradiated and non-irradiated solutions of **G1-Me** and **G2-Me** was the same as in the pristine solution of *L*-glutamic acid (Figure S1). The experiment was performed in triplicates.



Scheme S1. Synthesis of **G1-Me** and **G2-Me**.

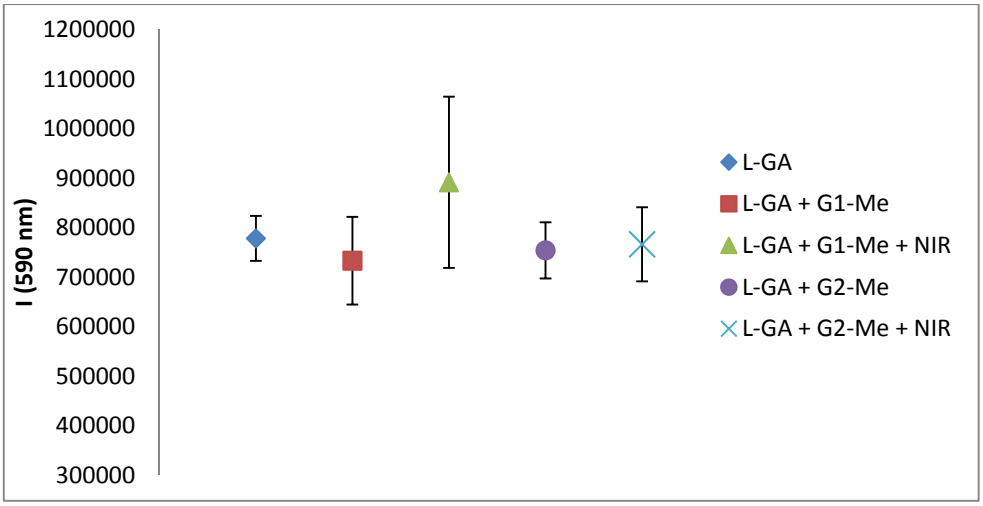


Figure S1. Detection of *L*-glutamic acid in the presence of **G1-Me** and **G2-Me**.

References:

1. N. Fomina, McFearin, C. L., Sermsakdi, M., Morachis, J. M., Almutairi, A., *Macromolecules*, 2011, **44**, 8590-8597.
2. T. Furuta, S. S. H. Wang, J. L. Dantzker, T. M. Dore, W. J. Bybee, E. M. Callaway, W. Denk and R. Y. Tsien, *Proc. Natl. Acad. Sci. U. S. A.*, 1999, **96**, 1193-1200.